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THE TANNINS.

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A MONOGRAPH ON THE HISTORY, PREPARATION, PROPERTIES, METHODS OF ESTIMATION, AND USES OF THE VEGETABLE ASTRINGENTS,

WITH AN INDEX TO THE LITERATURE OF THE SUBJECT.

BY

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PREFACE.

THE title of this monograph might well have been "A Century of Tannin," as just about one hundred years have elapsed since tannin first became recognized as a distinct substance, or class of substances, as we now express it. To emphasize this idea of a class of substances the present title was selected.

About twelve years ago the author commenced to collect a portion of the literature on the subject, especially that referring to the astringent value of certain tannin-bearing materials, with the methods involved in their estimation. He found, however, the task rapidly assuming such formidable proportions that only by beginning with the history and systematically pursuing the subject through its various phases to an ending, with a complete index to the literature, could he hope to reduce the many published inconsistencies and contradictions to a condition that would be available to himself as well as to others.

The taking of notes and references has been persistently carried on, especially during the past five years, until it is now thought best to give to the public the work on the general subject, with gallotannic acid, and the index to the literature, leaving for a subsequent volume the remaining individual tannins, with such further additions to the index as it may be found possible to collect.

It has been the constant effort of the author to make

this volume something more than a mere compilation of others' work, therefore some of his own experience has been incorporated which is here published for the first time, and this will be kept constantly in mind during the further contributions on the subject.

The tannins occupy a part of the border-land in science between botany and chemistry, which fact has added to the bulk of the literary index as well as to the difficulties of collecting it.

However, by the aid of the many complete sets of valuable foreign chemical periodicals recently acquired by the library of the Franklin Institute, and also through constant access to the library of the Philadelphia College of Pharmacy, it has been possible to take from the original sources all but about five per cent. of the titles given. Such references as could not be so consulted were taken from the most available source, and, if possible, in the same language as the original.

It is with the hope that information will be received from others interested in the subject, which will assist in making the index more complete, that it is issued at the present time.

Much valuable assistance has already been received by the author, especially from those having desirable private libraries, for which he hereby tenders his sincere thanks.

PHILADELPHIA, November 18, 1891.

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PART I.

GENERAL.

THE TANNINS.

SECTION I.

THE DISCOVERY OF THE TANNINS.

THE history of tannin as a proximate principle takes its beginning in France during the period between 1790 and 1800. Previous to that time the histories of leather, galls, and oak-bark are our only sources of information regarding the development which led to the discovery of tannin.

Great discoveries are rarely made without some warning; in reviewing their origin we see that they have had a gradual birth, and the exact date which indicates the beginning of their existence cannot be determined. In these evolutions of a discovery there are sometimes periods of comparative inactivity, succeeded by sudden and great advances. The history of tannin has not been an exception to the rule of gradual discovery, for we find among the earlier writers on the subject a disposition to attribute the astringency of galls and oak-bark to some peculiar principle, which, however, they did not separate or name.

Dr. William Lewis, in his "Philosophical Commerce of the Arts, London, 1763," calls attention to

the presence of a substance in certain vegetable infusions, which, when mixed with "green vitriol," produces "a deep black liquor, of most extensive use for dyeing and staining black. The power by which they produce this blackness and their astringency, or that by which they contract an animal fibre, seem to depend upon one and the same principle, and to be proportional to one another." "Of the properties of this colouring and astringent matter, little more is known than that it is dissolved and extracted from the subject both by water and spirit of wine, and that it does not exhale in the evaporation of the liquors by heat."

English writers on tannin usually ascribe to Dr. Lewis the honor of having a part in its discovery, but further than for writing the above quotation of facts, which were well known before his time, it is unreasonable to give him credit.

He was followed by other investigators, chiefly on galls and oak-bark, especially in the relation of the latter to tanning, which gradually led to the discovery of gallic acid by Scheele in 1786.

Dizé in 1791 repeated Scheele's experiments on galls, obtaining similar results; but he went further, and separated what he called a resinous substance by means of ether. It was unchanged on exposure to air, possessed an herbaceous taste, dissolved readily in water, and this sólution formed a white precipitate with sulphuric acid.

Two years later, in 1793, Deyeux, a French chemist and apothecary, published a memoir giving the results of an elaborate series of experiments, preceded by a description of the Aleppo and some other varieties of

galls. It is then stated that, "in the number of properties which appertain to nutgalls, there is one, very remarkable, which has always fixed the attention of chemists,—namely, the precipitate of the solution with the solution of iron salts. This has been attributed to an astringent body,—'*principe astringent.*'

"Among those who have occupied themselves with this subject may be mentioned Cartheuser, Rouelle, Macquer, Monnet, and Giannoti; but it is principally the academicians of Dijon, likewise Scheele, Berthellot, Fourcroy, and others, to whom we are indebted for the positive knowledge of this singular substance. They have demonstrated the existence of a peculiar acid which they have named gallic acid. This has made desirable a knowledge of the other constituents, and it is this which is made the subject of the following memoir."

The record of the experiments was made under eight sections, as follows:

1. "The action of water on nutgalls.
2. "The action of alkalies on the infusion and decoction of nutgalls.
3. "The action of alcohol and ether on nutgalls.
4. "Distillation of nutgalls with water.
5. "Dry distillation of nutgalls.
6. "Examination of the gallic acid which sublimes during the distillation of nutgalls.
7. "Examination of the precipitate which forms when nutgalls, their solution, and gallic acid are added to ferrous sulphate.
8. "Recapitulation."

This last section may be briefly stated as follows:

Nutgalls are composed of (1) a true extractive mat-

ter, (2) a peculiar resin, (3) a green coloring-matter, (4) gallic acid, (5) ligneous tissue. "All of these bodies except the ligneous tissue are in strong combination, resulting in a body soluble in alcohol, ether, and water. It is to this body entire and not to any principle in particular that the astringency belongs, since none of these compounds alone possess it."

In terminating this memoir the author expressed the hope that others would repeat his experiments and rectify his errors.

It has been quoted at some length because it is a record of experiments that for ingenuity and accurate reasoning would do credit to any investigator at the present time. The author was wrong in some of his deductions, but, when we consider that then all was darkness where now we have some light, it may not be far wrong to say that he came much nearer the truth than does many a one in our day when examining a new substance.

It is due Deyeux to say that he discovered tannin when he exhausted nutgalls with ether and described the product as a "refined dry and friable extract." On account of the gallic acid, he overlooked the possibility of there being a still more important substance present. All previous investigators had pointed so strongly to gallic acid as the principal constituent that, notwithstanding he found what he named a peculiar resin to be present in great abundance, he was unable or unwilling to realize it. Finally, he failed to distinguish between gallic and pyrogallic acids, but others also had failed to detect that difference.

We find at this time that the desire to improve the

process of tanning was the great incentive which led to a more exact knowledge of tannin. One of the chief objects in view was to shorten the process, and the idea of extracting the oak-bark or tan with water is usually attributed to Seguin, but previous to his patent was the suggestion of Macbride in 1795 to extract the bark with lime-water, and that of Anthony Fay to make an extract by boiling the tan with water in the proportion of one pound of the former to three gallons of the latter. This extract, or ooze, as he termed it, was to be weakened with water and used for tanning, which it accomplished in one-half the time occupied by the methods then in use. Fay's patent was dated January 17, 1790, although not published until 1796. Seguin's patent appears to have been dated in France in 1795 and in England in 1796, in the latter case under the name of William Desmond.

To afford an understanding of what bearing these patents, especially Seguin's, had on the discovery of tannin, it will be necessary to state that previous to his investigations the process of tanning was not supposed to be one of a combination of tannin with animal membrane, but simply a physical process in which the astringent property of the bark caused the hide to shrivel, harden, and become non-putrescible; therefore, when Seguin reasoned from his experiments, which were chiefly conducted on quite a large scale in the tanyard, that there was a principle present in oak-bark which combined with hide to form leather, he was given the credit of discovering tannin, although it had previously been separated and recognized as a distinct substance by both Dizé and Deyeux.

Seguin's conclusions were strengthened by the fact that, when he boiled hide with water and added to the clear cold liquid an infusion of oak-bark, he obtained a light-colored precipitate, which was insoluble in hot or cold water and became dark on exposure to light.

We derive our knowledge of Seguin's experiments from the report of a committee appointed to examine his process; after some months' investigation, during which time a hundred or more hides were tanned and the committee wore shoes made of the leather, a satisfactory report was made and published. The committee consisted of the citizens Lelievre and Pelletier.

Seguin's method of preparing the liquor was somewhat different from that of Fay. The latter, it will be remembered, boiled together the bark and water, while the former poured the liquor from one lot of ground bark to another until it reached a strength of from 10° to 12°. The advantage claimed for this form of the tanning material was that it could be transported, and, as the committee feared the early extinction of forests in France, they suggested that such an extract could be made in America.

The first separation of tannin in a pure condition was accomplished by Proust in 1798. He added a solution of stannous chloride to a decoction of galls, and produced an abundant yellow precipitate, which he stated to be a combination of the tanning principle with tin and free from gallic acid. The precipitate mixed with water and treated with hydrogen sulphide was decomposed, forming a sulphide of the metal, which precipitated, while the astringent principle remained in solution. After removing the sulphide by

filtration, the solution was evaporated in a silver basin, yielding a deep-brown, friable residue, which possessed the characteristic odor of the astringent principle. It had a vitreous fracture and did not attract moisture from the air. The taste was strongly astringent, and it completely dissolved in water and alcohol. The solution of this extract added to a solution of glue formed a magma which possessed the elastic properties of the gluten of flour, was perfectly insoluble in hot water, and was not susceptible of putrefaction. This the author believed to be the secret of Seguin's preservation of leather. The remainder of his interesting memoir was devoted to the effects of tannin and gallic acid on ferrous and ferric salts. He also pointed out the fact that the juice of sumac gave the same reaction as this compound from galls.

By these four investigators the existence of tannin was completely established, and gallic acid became of secondary importance as a constituent of galls and in tanning. It may be briefly stated that Dizé first indicated the existence of tannin and prepared it in an impure state, Deyeux prepared it in considerable quantity and recognized it as one of the important constituents of galls, Seguin considered it the tanning principle and put the knowledge of its existence to practical application, and Proust first prepared it in an almost pure state.

In 1801, Karsten reviewed the history of tannin, and attributed the discovery wholly to Seguin, although he spoke highly of Proust's work. It is very probable that his credit to Seguin was on account of the great practical importance of the latter's invention, which

gave it extensive publicity, while the more scientific works of Dizé and Deyeux were overlooked.

In 1802, Proust wrote another memoir on tannin, in which he concluded that there were many different kinds of tannin in different plants. This appears to be the first statement of what has since proved to be a most important principle in the study of the tannins, and with this work of Proust the history of the discovery of tannin may well be closed, and further historical considerations taken up under the individual members of the class.

SECTION II.

GENERAL CHARACTERS.

THE terms "tannin" and "tannic acid" are used indiscriminately by many writers, while others employ the term "tannic acid" to indicate the whole series and "tannin" to denote the product from oak-galls. It, however, appears more rational to apply the term "tannic acid" to the product from galls, since it is an acid when pure, and to use the term "tannin" to designate the whole class of astringent substances, many of which are glucosides, and many more hold an unknown position among the chemical compounds. Thus "tannic acid" will agree with the German *gerbsäure* and the French *acide tannique*, and "tannin" with the German *gerbstoff* and the French *tannin*, although many writers in those languages have also confused the respective terms. There is no objection to the use of a more exact designation by prefixing the source of the compound, as gallotannic acid to the product from galls, sumactannic acid to that from sumac, catechutannin to that from catechu, etc. In the following pages, therefore, the term "tannin" will be applied to the whole class of astringents, while the compound from galls, as well as those from other sources where they have been shown to be chemically and physically identical with it, will be designated by "tannic acid." In both cases a prefix indicating the source will be applied when necessary.

The tannins may be defined as a class of amorphous, astringent, vegetable substances, the members of which produce a blue or green color and precipitate with salts of iron, and with animal membrane form an insoluble and imputrescible compound called leather.

The tannins are widely distributed throughout the vegetable kingdom. The richest deposit appears to be in galls, of which they comprise from twenty-five to seventy-five per cent., according to the variety. The next most abundant source is the inner bark of certain trees, notably of the oak species; they are also found in leaves, unripe fruits, woods, and some buds and flowers, but rarely and in small quantity in seeds.

Many theories have been advanced by different investigators to explain the uses and method of formation of the tannins in plants. It has been observed that starch is always present with tannin in barks; that in many respects the tannins resemble the resins: the members of both classes, when heated with potassium hydrate, yield the same or similar products of decomposition, and, further, when seeds which are free from tannin germinate, it may then be detected. It has been found that the amount of tannin in a plant varies greatly with the time of year, and in some cases changes with the variation in the amount of starch present, as shown by Peacock in *Heuchera Americana*. He determined the amount of tannin to be greatest in October and least in May, while the starch was greatest in March. In *Geranium maculatum* it has been found by the author that the tannin is present in largest amount in April, just before the plant blooms, and rapidly decreases until it reaches a minimum in

October, thus pointing to the possibility of its being a storage material to assist the plant in blooming and perfecting its seed.

The questions which naturally arise from a consideration of the various facts are, Do the tannins result from the decomposition of starch? Are they closely related to the resins? Are they a reserve material, or simply a useless by-product? These problems remain to be worked out, and the answers may be found to vary with the kind of tannin. For instance, gallotannic acid is simply a morbid deposition of the compound resulting from the sting of an insect, while the other tannins vary according to the circumstances under which they have been formed.

Probably the most recent contribution to this subject, and one established on many experiments, is the monograph of Kraus, who has established some facts concerning the formation of tannin, but has not offered a solution of the various problems. He considered the tannins of different origin to be physiologically alike. This was stated soon after by Reinitzer to be incorrect. Kraus further found that light and carbon dioxide are essential agents of the formation of tannin in leaves. Leaves which are not green are not capable of producing tannin. The outer leaves of a plant, exposed to direct sunlight, contain more tannin than the inner leaves. It is not a product of the assimilation of chlorophyll grains; the oak, willow, and alder assimilate in dull weather without increasing in tannin. The tannin produced in the leaves passes into the branches and roots, and there is no experimental evidence that the tannin which has once passed into the rhizome undergoes further

change; there is rather an increase in the amount of tannin in the rhizome through a production in the dark. Kraus inclined to the belief that the use of tannin in leaves is either to protect them from being eaten or to prevent rotting, etc. Fallen leaves contain as much tannin as they did during their best time of growth, indicating that the leaf tannin is of no value to the plant. During the germination in the dark of seeds containing tannin, as oak and horse-chestnut, there is no diminution, but an increase, in the amount of tannin. There is not yet sufficient evidence to show whether tannin is produced from non-nitrogenous substances, or whether it is formed in the conversion of nitrogenous compounds into albuminoids. Finally, Kraus considered it probable that aromatic compounds may be formed in the production of albumen, some of which are used in the building up of albumen while others yield tannin. His investigations and conclusions rested on slight differences in the estimation of tannin, and Reinitzer claimed that the methods employed for the estimation of tannin are not sufficiently exact for physiological investigation. This is no doubt true of estimations made by different chemists, but one person should be able with the present methods to get results which are relatively accurate.

It was early suggested to divide the tannins into two classes,—the *iron-bluing tannins*, or those which give blue precipitates, and the *iron-greening tannins*, or those which give green precipitates with salts of iron. It has been found, however, that the same tannin may produce both blue and green precipitates with iron salts. Free acid, especially tartaric, causes the green color,

and, on the other hand, an iron-greening tannin may be changed to an iron-bluing one by the cautious addition of alkali.

A more recent and much more exact classification is that of Wagner into *pathological* tannins, those formed on vegetable tissue by the sting of an insect, and *physiological* tannins, those occurring in vegetable tissue. To the former class belongs gallotannic acid, and to the latter the great number of tannins found throughout the vegetable kingdom. The former give blue and the latter give both blue and green precipitates with salts of iron. It has been found that some of the latter class are identical with gallotannic acid; this was first pointed out to be true of sumactannic acid by Stenhouse, and was later confirmed by Löwe.

The method of preparing a tannin depends very much on the character of the material in which it occurs. Most of the published processes are based on the use of galls as the source, and a process available for exhausting them is not adapted to extracting a hard woody substance containing only five or ten per cent. of tannin. A process will, therefore, be given for each tannin, unless it can be referred to the following general method, which will be found available in many cases.

The finely-powdered material is packed in a percolator and extracted with commercial ether. The official ether of the United States Pharmacopœia, containing seventy-four parts ether, twenty-six parts alcohol, and a small quantity of water, gives satisfactory results; its specific gravity is very close to 0.750. The ether is recovered by distillation, the last portions being removed

under reduced pressure, and the residue is dissolved in such a quantity of water as will allow the solution to filter readily. This aqueous solution is distilled to dryness under reduced pressure, and the residue dissolved in a small quantity of water and rapidly distilled to dryness in as near a vacuum as possible, using in this, as in the preceding cases, a water-bath as the source of heat, when the tannin will "puff up" and remain as a light- or dark-brown residue, according to the character of the original material. It may then be purified according to the method given later for the purification of gallotannic acid. This process may be used for most substances which contain five per cent. of tannin or over; but it is well to bear in mind that there is no separation of the percolate into layers, as in the case of that from galls.

If less than five per cent. of tannin be present, it is more economical to extract with water and precipitate the tannin with lead acetate. The resulting lead tannate is then suspended in water, decomposed by hydrogen sulphide, and the filtrate from lead sulphide distilled to dryness under reduced pressure. Alcohol is sometimes used, but where the solvent can be recovered it has few if any advantages over ether. When economy is the first consideration hot water is used, and this will later claim especial attention under *tannin extracts*. In a few cases cold instead of hot water must be used or the impurities will predominate, as in the case of canaigre, which contains a large quantity of starch that is dissolved with the tannin by hot water and interferes with the use of the extract for many purposes.

Always when a pure tannin is desired heat and exposure to air must be avoided. Many plants appear

to contain two tannins; when such is the case it will sometimes be found that ether extracts one, and the other may then be removed by water, or occasionally cold water will extract but one and the other may then be removed by the use of hot water.

The tannins as a class are amorphous, odorless, slightly acid, and strongly astringent compounds, of a color varying from dark brown to pure white. They are, with few exceptions, soluble in water, alcohol, ether, and glycerin, and insoluble in chloroform, benzol, petroleum ether, carbon disulphide, fixed and volatile oils.

In addition to the above reactions given with iron salts, most if not all the tannins give brown precipitates with potassium bichromate. Lime-water gives precipitates, which, however, vary in color; at first they are white, but become rapidly darker, some red and others blue. Strong solutions of the alkaline carbonates also precipitate them. All the tannins are precipitated by gelatin or albumen; solutions of alum and ammonium chloride render the precipitation more complete. Saturated solutions of sodium chloride, calcium chloride, potassium acetate, and a number of other salts precipitate the tannins from solution; the same is true of moderately concentrated sulphuric and hydrochloric acids. Concentrated sulphuric acid dissolves the dry tannins with a yellow color, which on heating become dark-red rufigallic acid and then black metagallic acid. Nitric acid does not precipitate the tannins from solution, but it dissolves the dry compounds with a yellow color, and decomposes them with the formation of oxalic acid. Other oxidizing reagents, as potassium

bichromate and permanganate, decompose them very easily into carbon dioxide and some other unknown compound. When heated dry with arsenic acid, some of them are converted into ellagic acid. Most tannins are precipitated by alkaloids, notwithstanding the fact that both frequently exist in the same plant without forming an insoluble compound. The action of dilute acids and alkalies is one of considerable importance in determining their character; some, for instance, when heated to 100° with a one or two per cent. hydrochloric acid solution, yield crystalline compounds as gallic and ellagic acid, while others yield dark-colored amorphous compounds allied to the phlobaphenes; glucose is formed at the same time in nearly all the decompositions, thus showing their glucosidal nature.

Another method of determining the character of tannins is by the application of heat. When a tannin is heated to 120° no decided change takes place except a slight darkening in color; on continuing the heat the color gradually becomes darker, until at 160° decomposition takes place. With some tannins the products are metagallic acid and pyrogallol, and with others metagallic acid and catechol. It has been suggested to divide the tannins into two classes according as they yield, when heated, pyrogallol or catechol. Those which produce a brownish-colored deposit on leather, called "bloom," and form blue compounds with ferric salts yield, when heated, a sublimate of pyrogallol, while those which do not form a "bloom" on leather and give green compounds with ferric salts yield, when heated, a sublimate of catechol. To the former class belong the tannins from galls, sumac,

chestnut, and oak, and to the latter those from hemlock, catechu, rhatany, and mangrove. It is known not only that the tannins in the two classes have a different composition, but that most of those in the same class differ from one another in many particulars. In order to assist one in determining the character of a tannin it is necessary to study its decompositions by heat alone, by acids, and by alkalies.

Procter, in his "Text-Book of Tanning," and Allen, in his "Commercial Organic Analysis," have given similar schemes for carrying out these three processes.

The decomposition by heat may be effected by heating the sample in a small glass retort, but this is attended with considerable loss from a portion becoming overheated. The decomposition should take place by slowly raising the temperature from 160° to 215°, keeping it between 200° and 210° for twenty minutes. It has been suggested to assist the sublimation of the volatile products by leading a stream of carbon dioxide into the retort to carry them off as rapidly as formed.

Thorpe suggested a method of preparing pyrogallol for photographic purposes by heating gallic acid in glycerin as above directed, and this has since been applied to decomposing the tannins.

The details of the method are to heat one gramme of the tannin in 5 cc. of glycerin, slowly raising the temperature from 160°, and keeping it for from twenty to thirty minutes between 200° and 210°. It is then allowed to cool, 20 cc. of water are added, and the liquid is shaken with an equal volume of ether without previous filtration. The separated ethereal layer is evaporated to dryness and dissolved in 50 cc. of

water and tested for pyrogallol and catechol, according to the following:

	One per cent. Solutions of	
	Pyrogallol.	Catechol.
Ferric chloride . . .	Red color, turning brown.	Green color.
Ferric acetate . . .	Dark-purple color.	Green color.
Lime-water	Purple color, turning brown.	Clear red color.
Melting-point . . .	131°.	111°.
Pine wood moistened with HCl	No change.	Violet color.

The above tests will readily distinguish between pyrogallol and catechol when either occurs singly or mixed with only a small proportion of the other, but when they occur in a solution in nearly equal proportions it becomes a matter of much more difficulty. The tannin should be free from gallic acid and catechin before submitting it to the above operation, or else pyrogallol will be obtained from the former and catechol from the latter; this may be accomplished by thorough agitation of an aqueous solution of the tannin with ether and separation of the latter, the water is then rapidly distilled from the tannin under reduced pressure.

It has been found by the author, in carrying out the application of heat to tannins, that there is a practical difficulty in separating the ethereal layer containing pyrogallol and catechol when the 5 cc. of glycerin, after the application of heat, are dissolved in 20 cc. of water and agitated with ether. The emulsion formed

is difficult to get rid of. This may be overcome by agitating the 5 cc. of glycerin directly with 20 cc. of ether without first dissolving in water, or the sample of tannin may be heated with 5 grammes of paraffin, instead of 5 cc. of glycerin, and the paraffin dissolved in petroleum ether; the residue is then treated with water and agitated with ether, the ethereal solution separated as before, evaporated, and the residue dissolved in 50 cc. of water, when it is ready for testing.

In order to determine the effect of dilute acids on a sample, a convenient quantity of the latter is heated for an hour or more to 100° with a two-per-cent. solution of absolute hydrochloric acid. This may be accomplished by heating in a sealed tube or strong flask tightly stopped, or by attaching the open flask to an upright condenser and heating with a vigorously boiling water-bath. The solution, after sufficient heating, is allowed to cool, when a separation of insoluble matter indicates ellagic acid, anhydrides, or phlobaphenes. The mixture is filtered, if a separation has taken place, and the precipitate tested for ellagic acid by nitric acid, with which it forms an intense crimson color. The filtrate containing hydrochloric acid, undecomposed tannin, gallic acid, and glucose is agitated with ether to remove gallic acid, neutralized with sodium hydrate, and precipitated with basic lead acetate to remove coloring-matter and tannin. The excess of lead is removed with sulphuric acid, again neutralized with sodium hydrate, and the clear filtrate heated with an excess of Fehling's solution. The formation of a red precipitate of cuprous oxide indicates the presence of glucose.

The ethereal solution which removed gallic acid is evaporated, the residue, dissolved in warm water, allowed to cool, and filtered, when gallic acid, if present in the filtrate, may be detected by the red coloration produced by the addition of a few drops of potassium cyanide solution.

Since glucose occurs as a mixture in most tannins, it is necessary first to get rid of it before applying the above process. This may be accomplished by repeated purification of the tannin by precipitation with lead acetate; but such a process is very slow and tedious: so it has been suggested to use the lead salt for heating with the acid, in which case the sediment which separates when the liquid cools will consist in part or all of lead chloride, which may be collected on a filter with the ellagic acid and treated with boiling water, in which the lead chloride will dissolve.

It has been found by the author that the shortest method is to determine the amount of glucose in a tannin by removing the latter with lead acetate, and the excess of lead with hydrogen sulphide. The filtrate is then heated on a water-bath until every trace of hydrogen sulphide is driven off, neutralized with sodium hydrate, filtered, and the glucose estimated in the filtrate gravimetrically with Fehling's solution. Another portion of the sample is then heated with hydrochloric acid, and, after carrying out the process of hydrolysis, the glucose is estimated. Any excess of glucose in the second estimation over that in the first indicates that much glucose existed in the tannin as glucoside.

The action of alkalies is determined either on a sample

of the tannin or on the anhydrides and phlobaphenes resulting from the action of hydrochloric acid. This process of heating the tannins with alkali converts some of them into protocatechuic acid and either phloroglucol or acetic acid,—to this class belong the catechol tannins. Another class are converted into gallic and ellagic acids by the alkali, and they are found to be the pyrogallol tannins. The operation is carried out by taking 20 grammes of the sample and boiling for three hours with 150 cc. of potassium hydrate solution, specific gravity 1.20; the liquid is then concentrated with constant stirring until it becomes pasty. It is then cooled and neutralized with dilute sulphuric acid, filtered from the potassium sulphate, and the filtrate treated with sodium bicarbonate until the acid is neutralized. The liquid is agitated successively with several portions of ether; the latter, after separation, is recovered by distillation, and its residue dissolved in water; from this solution protocatechuic acid is removed by lead acetate, filtered, and the phloroglucol, when present, removed from the filtrate by ether; the latter is evaporated, and the phloroglucol is recognized by its sweet taste, by ferric chloride, which imparts to its aqueous solution a deep violet-red color, and by bromine-water, which causes a separation of crystalline needles, with evolution of heat and a very irritating odor.

With these various characters of the tannins our knowledge of them almost ceases. Except gallotannic and quercitannic acids the individuals have not been much studied, and the latter are only now in course of investigation by Böttinger. As recently as 1881, Darton, who has had considerable experience in the assay of

various tannin materials, ventured to repeat the conclusion of the older chemists that we have but one tannin, and that the differences are due to the other materials with which they are associated in the plant. It is true that one is often led, during the practical study of the subject, to ask whether we have more than one tannin or not, but this question is being answered as the study into the constitution of the various members is prosecuted. No doubt some relationship governing them exists, just as there is among the sugars, but as yet it has not been made out, and the study will necessarily be a long one, since there are so many individual tannins to be investigated. The problem will undoubtedly be worked out by a study of the derivatives, and this by means of bromine and acetyl has been well commenced on the gallotannic and quercitannic acids. We must keep in mind that a number of the individual tannins will be proved to be identical, as has been shown to be the case with sumac and a few others in regard to gallotannic acid, but with the great majority our present knowledge leads to the belief that a relationship only is to be worked out.

In general it may be said that the tannins are used in medicine, in the manufacture of leather and ink, and as a mordant in dyeing, but the special properties of the different members adapt them to a great number of minor uses. By far the largest amount of tannin is used in an impure state,—that is, in the form of an infusion or decoction, or as an extract, made by concentrating these solutions.

SECTION III.

THE DETECTION AND ESTIMATION OF THE TANNINS.

THE simple detection of the tannins is comparatively easy. A few tests applied to an infusion of the plant or substance serve to decide their presence or absence.

Ferric acetate or chloride is usually first employed, when a green or blue color and precipitate indicate tannin. Ferrous salts, when free from ferric, cause no change with tannin solutions unless the latter be concentrated, when a white gelatinous precipitate is formed, rapidly becoming dark on exposure to air. Potassium dichromate forms brown precipitates with nearly all tannins. Ammoniacal copper sulphate forms precipitates of different shades of color; but, according to Procter, the tannin of Hungarian larch is not precipitated by this reagent, and it does form insoluble compounds with some substances other than the tannins. Allen recommends an ammoniacal solution of potassium ferricyanide, which produces with the tannins a deep-red color changing to brown, even in very dilute solutions. Most of the alkaloids, when not in too dilute solution, produce whitish precipitates with the tannins. Calcium hydrate produces a whitish precipitate rapidly turning blue with gallotannic, but red with some other varieties, notably that from mangrove. An aqueous solution of iodine in potassium iodide, mixed with a small quantity of ammonia previously

diluted with ten times its volume of water, will produce a brilliant red color with solutions of the tannins, even when highly diluted.

Other characteristic tests for the tannins will be found under the chemical properties of the different varieties.

The methods for the quantitative determination of the tannins may conveniently be considered in four groups:

1. Miscellaneous methods, not belonging to any of the following.
2. Precipitation by metallic salts.
3. The gelatin or hide methods.
4. The permanganate methods.

1. Under the first class is the process of Commaile, which was based on the reduction of iodic acid by tannin in the presence of hydrocyanic acid. The iodic acid not consumed was estimated by reduction with sulphurous acid and precipitation by silver nitrate. This method has been unfavorably criticised by Cech and by Watts.

F. Becker suggested the use of methyl violet, 0.250 gramme in one litre. This was standardized by a one-per-cent. tannin solution, and it could then be used on tannin solutions of unknown strength.

Mittenzwey recommended a process in which the volume of oxygen absorbed by an alkaline solution of tannin was measured. Cech found this to give unsatisfactory results, but Watts, after improving some details in the apparatus, considered it a fairly accurate method.

Wagner proposed titrating the tannin solution with cinchonine sulphate, using rosaniline acetate as an indi-

cator. This method failed to give satisfaction, on account of the difficulty in determining the end of the reaction. Clark used a modification of this for the estimation of tannin in tea. His improvement consisted in adding an excess of the cinchonine sulphate, filtering, and estimating the excess of the alkaloid by titrating with potassio-mercuric iodide. A series of trials, by the author of this volume, in which the method was tried on gallotannic acid, failed to give concordant results.

F. Musset suggested using an excess of standard solution of iodine, and, after twelve hours' standing, titrating the free iodine with standard sodium thiosulphate, which was added in excess and titrated with decinormal iodine solution and starch.

2. The methods of precipitation with metallic salts are very numerous and comprise many modifications. It is desirable sometimes to obtain the value of a tannin by this means, therefore the following more important processes will be given.

Pribram in 1866 detailed a method involving precipitation by lead acetate, washing, drying, and weighing the precipitate; but, as there are at least three salts of lead tannate, according as the lead acetate or tannin is in excess, and these salts are readily decomposed by washing, it is evident that such a method can only give approximations.

Allen originated a modification of this for assaying the tannin in tea, in which the latter in hot concentrated solution was titrated by a volumetric solution of the lead acetate; the end of the reaction was ascertained by filtering a small portion of the liquid and testing with

ammoniacal potassium ferricyanide, which gave a red color turning brown as long as any uncombined tannin was present. As stated by its author this estimation included gallic acid, so would not be available for all cases.

Dragendorff[1] recommended that precipitations with lead acetate should be carried out in moderately concentrated solutions, avoiding an excess of the lead salt and not continuing the washing too long.

R. Jackson suggested the use of lead carbonate with which to agitate the tannin solution. The specific gravity before and after the treatment giving the loss of tannin, a difference of .0038 indicated one per cent. of tannin.

For the estimation of tannin in plant analysis Dragendorff recommended estimating the tannin soluble in absolute alcohol, after replacing the solvent by water, by precipitating with lead acetate, rapidly washing, drying, and weighing the precipitate, which was then burned and the residue of lead oxide subtracted from the original weight. This operation was then repeated with copper acetate. When the amount of organic matter precipitated by each was equal, the substance was assumed to be tannin; but, in case the lead salt precipitated more than the copper salt, the organic matter obtained by the latter was taken as representing the amount of tannin, while the excess obtained by lead acetate over that by copper acetate was reckoned as other organic acids and coloring-matter.

Copper acetate appears to have been first suggested for the quantitative determination of tannin by Sakur.

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[1] Plant Analysis, English edition, p. 41.

The precipitate with it, like that of the corresponding lead salt, is not of constant composition; therefore the precipitation must be made with moderately concentrated solutions, and the resulting precipitate rapidly washed, dried, and weighed. Fleck precipitated the tannin by copper acetate, and washed the precipitate with ammonium carbonate to remove gallic acid. The precipitate was then washed, dried at 100°, weighed, and ignited. Wolff found 100 parts of cupric oxide represented 130.4 parts of tannin.

Pavesi and Rotondi found 100 parts represented 145 parts tannin. This difference among different investigators Schiff explained by supposing they used tannins of variable degrees of purity, and he found 136 parts of pure digallic acid to be represented by 100 parts of cupric oxide.

J. Persoz recommended dissolving eight grammes of ammonium chloride in one litre of water, and in this dissolving some stannous chloride. Ten grammes of pure dry tannin were then dissolved in one litre of water, and 100 cc. of this solution precipitated with 100 cc. of this stannous chloride solution, the mixture allowed to stand ten or twelve hours in a graduated cylinder, and the volume of the precipitate read. Then ten grammes of the tannin material were boiled for one-half hour with a half-litre of water, filtered, and the residue washed with sufficient water to make one litre; 100 cc. of this solution in a similarly graduated cylinder were then precipitated with 100 cc. of the stannous chloride solution, and after standing ten or twelve hours the volume of the precipitate was compared with that from the pure tannin.

Risler-Beunat proposed to modify the method by collecting the precipitate of tin tannate, washing, drying, and igniting, with the addition of a little ammonium nitrate in order to completely convert the residue into stannic oxide. The weight of this residue was converted into tannin by a calculation based on the amount of residue obtained from a pure dry tannin. Dragendorff found that the precipitation was incomplete, that it took place slowly, and that the precipitate was partly decomposed by washing.

Gerland suggested the use of tartar emetic in the presence of ammonium chloride for the volumetric estimation of tannin; the method, however, met with little favor until improved by Richards and Palmer, who used ammonium acetate instead of the chloride, both of which prevent the precipitation of gallic acid and assist the precipitation of the tannin. The tartar emetic was dried at 100°, and then used in the proportion of 6.730 grammes in one litre; in such a solution 1 cc. corresponded to 0.010 gramme of digallic acid. The ammonium acetate was made by saturating glacial acetic acid with strong solution of ammonia, and 1 cc. of this solution added to every 25 cc. of the tannin solution, which latter should contain from 0.1 to 0.3 gramme of tannin in every 100 cc. Three or four tests should be made in as many beakers placed side by side, and the end of the reaction determined by placing a drop of the clear supernatant liquid on a white porcelain surface, adding a drop of sodium thiosulphate, and warming; a red color of antimony sulphide will form when the least excess of the reagent has been added.

Ammoniacal zinc acetate was recommended by

Terreil in 1874, by Carpenè in 1876, and by Barbieri in 1877. While the details of the different authors varied somewhat, the following covers most of the methods. The reagent was added to a boiling solution of the tannin, and the mixture concentrated to one-half, when it was cooled and filtered. The precipitate was dissolved in dilute sulphuric acid, and the tannin estimated by titration with potassium permanganate. This process was especially recommended for determining the tannin in wine, but Dragendorff found it of little value.

Handtke used ferric acetate in the presence of sodium acetate, and found it available for the estimation of the tannins of oak-bark, valonia, dividivi, sumac, and catechu, when the concentration was such that the precipitate yielded 45.8 per cent. of ferric oxide by ignition; but with a number of tannins it did not yield satisfactory results, and the process is apparently not used.

3. Methods of estimating tannins by means of gelatin, isinglass, and hide or hide powder have been suggested in great number, with as many or more modifications by others until the list is a formidable one. Apparently the first paper on the quantitative determination of tannin was by George Biggin in 1799, who collected, washed, dried, and weighed the precipitate produced by gelatin on tannin. He did not attempt to arrive at the exact amount of tannin present, as he made no estimation of the value of the precipitate in tannin. It could, therefore, be used only to compare one material with another, and was available only to the tanner who wished to compare the value of a new substance with that of a well-known one he was using.

Davy in 1803 extracted six parts of bark with

water and precipitated it with one part of isinglass, washed, dried, weighed the precipitate, and calculated 40 per cent. of it as tannin.

Müller suggested the addition of alum to the isinglass or gelatin solution, and a solution of three grammes gelatin and one gramme alum in one litre of water is largely used at the present time in two modifications,—one to collect, wash, dry, weigh the precipitate, and reckon 54 per cent. of it as tannin; the other to use the solution volumetrically and determine the end of the reaction by filtering off a small portion of the solution and testing until no further precipitate is caused by the reagent. The solution of gelatin and alum must first be standardized by a solution of pure tannin. Notwithstanding the objection to this method, and the fact that we have many others for which greater accuracy is claimed, it continues to be used, and, no doubt, in careful and experienced hands will yield uniform results.

The following details of this process have been employed by the author for several years with considerable success. The results have in most cases agreed closely with those obtained by the permanganate method. The solution is made of 2.5 grammes gelatin and 10 grammes alum in one litre. This solution, as well as that of the tannin, is warmed to 70°. The reagent is then dropped in with constant stirring until the precipitate coagulates and leaves a clear supernatant liquid which gives no further precipitate on the addition of a few drops of the reagent. In case the coagulation does not take place so as to furnish a clear liquid and one that filters easily, the whole should be

thrown out and a more dilute solution of the tannin material taken. When precipitation has taken place satisfactorily, the mixture should be rapidly poured on two counterpoised filters placed one inside the other, the precipitate washed with just sufficient warm water to remove alum, dried at 110°, and weighed. For gallotannic acid 54 per cent. of the precipitate should be considered tannin. With the amount of alum above mentioned it is possible to add the gelatin solution in slight excess without dissolving any of the precipitate.

According to Johanson 100 parts of gelatin precipitate 120 parts of dry tannin.

Schulze recommended the use of ammonium chloride to cause coagulation of the precipitate; his solution contained ten grammes of gelatin in one litre saturated with ammonium chloride, and Löwenthal used a saturated solution of common salt with one-tenth its volume of hydrochloric acid (specific gravity 1.120) for the same purpose, but, if the proportion of alum (10 grammes to 1 litre) recommended above be used and the details carefully carried out, it will be found preferable.

Powdered or rasped raw-hide was originally suggested by Davy and more recently used in the process of Hammer. This method consisted in preparing a solution of the tannin material, taking its specific gravity, then digesting it for a few hours with hide to four times the supposed amount of tannin present, which latter should be present to the extent of from 3 to 5 per cent., filtering, and again taking the specific gravity. The loss in specific gravity on account of digesting with hide represented the tannin, a loss of .0040 indicating one per cent.

There are many sources of error in this process, as has been pointed out by Rau, who says, "A 5-per-cent. solution of gallotannic acid had a specific gravity of 1.01841. The density of distilled water being 1.0000, the 5 per cent. gallotannic acid was represented by the increase in specific gravity 0.01841. A solution of cane-sugar was prepared having specific gravity 1.01646, and 5 per cent. of the same gallotannic acid dissolved therein. The specific gravity of the latter solution was then found to be 1.03398; consequently the same percentage of tannin was in this case represented by a somewhat smaller increase in specific gravity, 0.01752." The same author by experiments showed that the coloring-matters of logwood and Persian berries were largely absorbed by the hide powder along with the tannin.

Simand recommended the use of bone tissue instead of hide powder. This bone tissue he prepared by taking tubular bones free from joints, macerating them for two days with a five-per-cent. solution of soda, thoroughly washing with water, reducing to smaller pieces, and treating with dilute hydrochloric acid until softened, then washing and passing through a grinding machine while still wet. This comminuted mass was treated with dilute hydrochloric acid, thoroughly washed, pressed, and dried.

Simand and Weiss estimated the tannin in extracts by hide powder, which they prepared from fresh skin by washing, unhairing, treating with dilute hydrochloric acid, stretching, and drying. The skin was then planed fine, dried, and worked through a fine sieve. The watery residue from 5 grammes of this powder

gave only 0.036 gramme dry residue, containing 0.008 gramme ash.

In order to estimate a sample of tannin extract, from 12 to 16 grammes of a solid or 22 to 28 grammes of a liquid sample were taken, dissolved in distilled water, made up to one litre, and filtered; 100 cc. were evaporated to dryness, dried, and weighed, thus giving the total amount of soluble matter; 250 cc. of the solution were placed in a dry flask with one gramme of hide powder and shaken for two hours, then filtered into another flask and this treatment with one gramme of hide powder twice more repeated, and then a fourth time with 2 grammes of hide powder. This quantity (5 grammes) was considered quite sufficient to extract all tanning material. The solution was then filtered for the fourth time and 100 cc. evaporated and dried. The difference between this weight and that obtained by the first evaporation indicated the amount of tannin.

Bone tissue as well as hide powder is available for this process, which has many points of value, and, if the correction for the solubility of the hide powder or bone tissue could be accurately made, it would be the most satisfactory and exact of the numerous methods that have been proposed. In actual practice, however, it has been found almost impossible to get a gelatinous tissue that is not somewhat soluble in water, which solubility should be added to the amount of tannin found, but, as most of the soluble portion is capable of being precipitated by tannin, it is not proper to add the whole amount of tissue which is dissolved by water, therefore the correction is an unknown quantity, and,

unless a gelatinous tissue can be made that is completely insoluble in water, the process is not available.

Muntz and Ramspacher contrived an apparatus for use in Hammer's method, which consisted of a press so constructed that the tannin solution could be forced through hide, the specific gravity taken before and after, or a portion of the liquid evaporated in each case. It, however, had no advantages over the original method, and has been used but little.

4. Under the fourth class of methods we have practically one in which the use of potassium permanganate is combined with the gelatin or hide method. The use of calcium hypochlorite has been suggested to replace the permanganate, but with no apparent advantage.

Monier in 1858 first proposed the use of potassium permanganate for volumetrically determining the amount of tannin by adding the reagent until the solution assumed a pinkish color. It was soon found, however, that tannin was not the only substance oxidized by permanganate, and in infusions the color interfered with the determination of the end reaction.

In 1860, Löwenthal rendered the process more available by suggesting the use of indigo as an indicator, which at the same time controlled the oxidation, and this he further greatly improved in 1877 by combining the gelatin process with it, making a permanganate valuation, before and after treatment with gelatin. Neubauer in 1871 suggested a similar improvement, using animal charcoal instead of gelatin.

The permanganate method, with further improvements by Procter, Hunt, Von Schröder, Councler, and others, has come to be regarded as the standard process

of the present time, although it is not without its faults, and is especially difficult for one who only occasionally desires to make a tannin assay.

In 1883 a Commission of German technical chemists was appointed to meet in Berlin and report on a method of tannin assay. This Commission consisted of Dr. C. Councler, Dr. J. v. Schröder, and Messrs. A. Eberz, Franz Kathreiner, Schaun, and F. Simand. W. Eitner, of Vienna, was prevented from taking part in the proceedings. In two years they presented a report, under the title of "Bericht über die Verhandlungen der Commission zur Feststellung einer einheitlichen Methode der Gerbstoffbestimmung, Cassel, 1885. Verlag von Theodor Fischer." In addition to the recommendations, this report contains a critical investigation of the Löwenthal method by Dr. von Schröder.

The following process will give that recommended by the Commission, together with some improvements that have been suggested by various investigators since. Although far from perfect, it may be said to represent fairly the method of to-day, and is capable of giving satisfactory results in competent hands.

Briefly outlined, the process, which is still known as Löwenthal's, consists in taking a dilute solution of potassium permanganate, determining the amount of it necessary to decolorize or change to yellow a given amount of indigo solution, and then the amount required to change the same volume of indigo solution and pure tannin solution. Another portion of the tannin solution is then treated with gelatin or hide powder, filtered, and portions of the filtrate and indigo which represent the same amounts as were previously

treated with permanganate are again decolorized by that reagent. The difference in volume of permanganate solution used before and after treatment with gelatin gives the amount of permanganate required to oxidize this known amount of tannin.

This tannin solution can then be replaced by an infusion which represents a known quantity of tannin material, and the percentage readily calculated. The indigo serves as an indicator and at the same time controls the oxidation; since it is decolorized with some difficulty, it indicates that the other substances have all been oxidized when the blue color disappears.

SAMPLING AND PREPARATION OF THE TANNIN INFUSION.

From 500 to 1000 grammes are so taken as to represent the whole cargo. This sample is then ground in a drug-mill or powdered in a mortar until all of it will pass through a sieve of 20 meshes to the inch. It is not sufficient to discontinue the grinding when enough has been obtained to furnish 10 or 20 grammes for the infusion, but the whole 500 or 1000 grammes must be ground, sieved, and then thoroughly mixed before proceeding, since the first portion ground is much softer than that reduced last, and therefore represents a different amount of tannin. After all has been ground, sieved, and thoroughly mixed, 5 grammes of galls, 10 grammes of sumac, valonia, or myrobalans, or 20 grammes of bark are boiled for one-half hour with 500 cc. of water, strained into a litre flask, and washed and pressed with sufficient water to bring the measure of the infusion to one litre.

As glass is liable to fracture in the above boiling, a kettle of what is known in this country as "agate-ware" has been found very satisfactory. The infusion may also be prepared in an apparatus described by Von Schröder (Fig. 1), which consists of a cylindrical

FIG. 1.

cast-tin vessel 12.5 cm. high and 7 cm. in diameter, with a spout but no handle; the latter is omitted in order that the vessel may be more readily heated in a water-bath. Accompanying this is a strainer or plunger of the same metal, with a handle about 16 cm. in length. The strainer is of such diameter that when covered with muslin it will just fit the inside of the cylindrical vessel and play the part of a piston to it. Five, ten, or twenty grammes of the powdered material are placed in the vessel, 200 cc. of cold distilled water added, and,

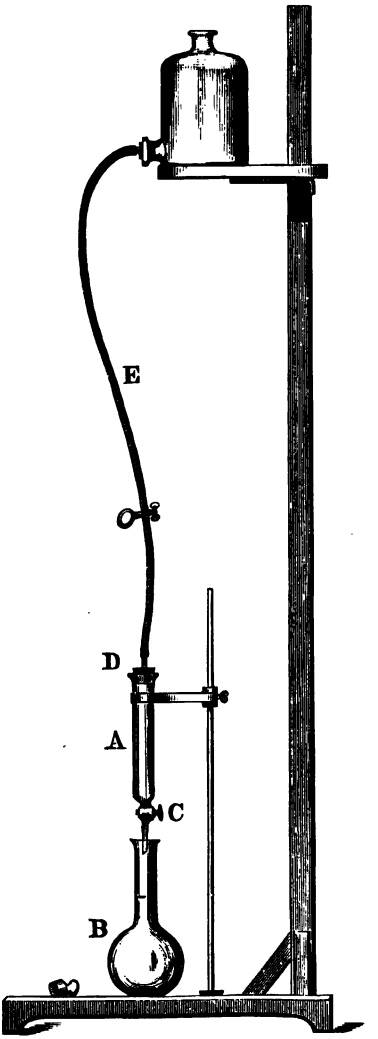
after macerating for one hour, the strainer is pressed into the cylinder and the solution poured into a litre flask. The strainer is then drawn up, and, without removing it, 200 cc. of hot distilled water are poured in so as to wash the liquid and powder adhering to the strainer down into the vessel, which is immediately set in a water-bath and heated for one-half hour, the strainer pressed down, and the solution poured into the litre flask. This operation of hot extraction is continued until 1000 cc. of infusion are obtained; it is then allowed to cool, cold water is added to bring the solution again up to the mark, and the whole is filtered. The tannin strength of the solution should be such that 10 cc. will not reduce more than 8 cc. of permanganate solution.

It is sometimes desirable to distinguish between the *easily* soluble tannin and the *difficultly* soluble tannin. That which dissolves in cold water is accepted as representing the former, while that which is *afterwards* removed by hot water represents the latter. The infusion of these may be prepared by extracting in the Von Schröder apparatus with cold water until one litre is obtained, and then preparing a litre of the hot infusion from the residual material.

It was suggested by the Commission to employ a Real's press for the cold extraction of the tannin material. This consists of a closed cylindrical percolator of metal so arranged as to allow the water to be applied under the pressure of a column one and one-half metres in height.

The accompanying illustration (Fig. 2) is of an apparatus which may be constructed in any laboratory,

FIG. 2.



and will accomplish the purpose under any reasonable height of water column. This consists of a glass percolator, *A*, fitted with a stopcock, *C*, at the lower end, and with a tightly-fitting rubber stopper, *D*, at the top; to a glass tube in this cork is attached a rubber tube, *E*, of any desired length, and connected with a small reservoir, that is arranged to be placed at variable heights above the percolator, and at the lower orifice of the latter is placed the litre flask *B*. The sample is packed in *A* and cold distilled water run on until it begins to drop from the lower end, the stopcock *C* is then closed, and under a pressure of a column of water one and one-half metres in height it is allowed to macerate for from twelve to sixteen hours; the stopcock is then opened, and the percolation allowed to proceed until one litre of liquid is obtained. The liquid should not be allowed to come from the percolator faster than in drops, and to obtain one litre should require from three to four hours. It is just as well to have a pinch-cock attached to the rubber tube *E* to assist in controlling the flow of liquid. When the desired amount of cold infusion has been obtained, the residue is extracted with hot water in a Von Schröder apparatus or any other convenient vessel in order to obtain one litre of the hot infusion.

THE ASSAY OF THE TANNIN INFUSION.

For this part of the operation the following apparatus and chemicals are required.

1. *Permanganate Solution.*—Ten grammes of pure potassium permanganate are dissolved in 6 litres of water.

2. *Indigo Solution.*—A solution of 30 grammes of sodium sulphindigotate ("Carminum cœrul. opt., pure Indigotin I. of Gehe and Co.," Dresden) in 3 litres of dilute sulphuric acid (1 volume of the acid to 3 volumes of water). This is agitated for some time, filtered, and sufficient water added through the filter to make 6 litres. The value of this solution should be such that 20 cc. in 750 cc. water should require about 10.7 cc. of the above permanganate solution to decolorize it.

3. *Hide Powder.*—This must be white and woolly in character, and not yield to cold distilled water any substance capable of reducing permanganate. Such a powder is prepared by Dr. Roth, of Berlin, and by the Vienna Research Station, and can usually be had of importers and dealers in chemicals throughout the world.

4. *Standardizing the Permanganate Solution.*—The purest obtainable tannin (that of Schering was recommended by the Commission) is used for the standard. For this purpose a portion is dried at 100° to constant weight, then such a quantity of the air-dried substance as to represent 2 grammes of it in the dried condition is taken and dissolved in one litre of water.

10 cc. of this solution and 20 cc. of the indigo solution are added to 750 cc. of water, and the permanganate solution is run in from a graduated burette with constant stirring until the liquid assumes a greenish color, and then more cautiously, a drop or two at a time, until a pure yellow color with a pinkish rim is reached, which is most apparent on the shaded side. 50 cc. of the tannin solution are then macerated with 3 grammes of hide powder (which has been previously well moistened and

squeezed out) for eighteen or twenty hours with frequent agitation, filtered, and 10 cc., with 20 cc. of indigo solution in 750 cc. of water, titrated with the permanganate as before. The difference between the amount of permanganate in the first and second titrations represents the tannin or oxidizable matter removed by hide. The "not tannin," or oxidizable matter not removed by hide, should not much exceed 5 per cent.

The titration is best carried out in a porcelain dish, although a beaker-glass on a white surface may be used.

Having the value of the permanganate in tannin, we next take the infusion prepared as previously described and carry out the titration with permanganate and treatment with hide on it, by using 10 cc. of the infusion, 20 cc. of the indigo solution, and 750 cc. of water. After obtaining the permanganate value of this infusion, 50 cc. more of the latter are agitated for from sixteen to eighteen hours with 3 grammes of hide powder as before, and 10 cc. of the filtrate titrated in the presence of 20 cc. of the indigo solution and 750 cc. of water. From these data it is easy to calculate the percentage of tannin in the material from which the infusion was made.

Von Schröder found by the use of Hammer's method that the pure tannin does not represent the full value of the tanning material, and suggested that the tannin found be multiplied by 1.05.

Neubauer used animal charcoal instead of hide powder for absorbing the tannin; it has been found, however, to absorb other substances than tannin in considerable quantity.

Löwenthal used a solution of gelatin instead of hide powder. This solution was prepared by taking 20 grammes of good gelatin, allowing it to swell for several hours in cold water, then dissolving with the aid of heat and more water, saturating the solution with common salt, adding 100 cc. of hydrochloric acid and sufficient water to make one litre. The infusion after agitation for some time with the gelatin solution was found to filter slowly, and Procter suggested stirring in about 5 grammes of finely-powdered kaolin for causing a rapid settling of the precipitate and so giving a solution which filtered rapidly and clear.

Simand recommended the bone tissue previously described.

Many more details and numerous suggestions of minor importance might be added, but they would serve rather to complicate the process given. To those who wish to study the original papers on tannin estimation more in detail, the following are recommended: Gauhe, Cech, Löwenthal, Neubauer, Procter, Nötzli, and the Report of the Commission of German chemists.

PART II.

GALLOTANNIC ACID.

SECTION I.

SOURCES.

By the puncture of a small insect, the *Cynips Gallæ tinctoriæ*, on the young buds of the small twigs of *Quercus lusitanica*, variety *infectoria*, there are deposited ova, around each of which rapidly forms a mass that in its perfected state becomes the gall, oak-gall, or nutgall of commerce. The small tree or shrub which furnishes these galls grows chiefly in Asia Minor and some of the other regions surrounding the Mediterranean Sea.

The early history of galls is conveniently assigned to the ancients. Hippocrates administered them medicinally, and from the earliest times they were resorted to as a means of staining the hair black. Theophrastus, Dioscorides, Pliny, and other writers mention the superiority of the galls from Syria.

The most esteemed galls at the present time are those collected in Mesopotamia and shipped from Bombay to London. They are known in commerce as Levant galls. The best-known variety in this country comes under the name of Aleppo or Turkish galls. They are collected in the surrounding districts and taken to Smyrna, where they are sorted and shipped to various

parts of the world. Poorer varieties are shipped from some other Mediterranean ports.

Galls are nearly globular, from ten to twenty millimetres in diameter, tapering slightly towards the base, the lower half being smooth, while the upper portion is usually covered with numerous bluntly-pointed tubercules. The best galls are gathered before the insect has matured; if left until after this development has occurred, there is found about half-way between the stem and summit a small hole, from which the developed insect has escaped; at this period they are found to be deficient in tannin, and therefore become the green or white variety. Those collected at the proper time are heavy, somewhat brittle, breaking with a slightly resinous fracture, exhibiting the larva in a small cavity at the centre, while the surrounding tissue frequently appears as a radiating structure. Internally galls are deep greenish yellow, without odor, of a slightly acid and very astringent taste with a faintly sweetish aftertaste.

When Scheele in 1786 discovered gallic acid he supposed it to be the most important constituent; Chevreul afterwards found ellagic acid; then Scheele produced pyrogallic acid, and supposed it identical with gallic acid, but much purer, on account of having been sublimed; then followed the work of Dizé, Deyeux, Seguin, and Proust, as stated in the preceding general history.

After the existence of tannic acid was well established, Davy in 1803 appears to have been the first to make an analysis of nutgalls, with the following result:

Tannic acid	26.00	per cent.
Gallic acid	6.20	"
Gum and insoluble tannin	2.40	"
Calcium and other salts	2.40	"
Woody fibre	63.00	"
	100.00	"

These figures indicate either that the quality of the galls was poor, or, more probably, that the methods in use at that time were defective.

A more recent analysis was made in 1845 by Guibourt, with the following result:

Tannic acid	65.00	per cent.
Gallic acid	2.00	"
Ellagic and luteo-gallic acids	2.00	"
Chlorophyll	0.70	"
Brown alcoholic extract	2.50	"
Gum	2.50	"
Starch	2.00	"
Cellulose	10.50	"
Sugar, albumen, Sulphate of potassium, Chloride of potassium, Gallate of potassium, Gallate of calcium, Oxalate of calcium, Phosphate of calcium	1.30	"
Water	11.50	"
	100.00	"

These results have been generally accepted, and are universally quoted in text-books, as no chemist since then has attempted such a detailed analysis. It may with reason be doubted if an analysis at the present time would agree in all points with this one.

A still more recent, although not intended to be so

complete an examination was made in 1869 by Watson Smith, for the purpose of comparing English and Aleppo galls:

Tannic acid	61.65	per cent.
Gallic acid	1.60	"
Woody fibre	15.68	"
Water	12.32	"
Coloring-matter and loss	8.75	"
	100.00	"

Another variety of galls, which for some purposes rivals the Turkish in importance, is that from China. These are formed by an insect, *Aphis Chinensis*, on the leaf-stalks and young branches of *Rhus semialata*, a tree from ten to fifteen metres in height, indigenous to North India, China, and Japan. Chinese galls are hollow, from two and a half to four centimetres in length and half that measure in breadth. They are frequently quite irregular in shape, with horn-like projections. The shell, which constitutes the material part, is thin and brittle, breaking with a resinous fracture. The external surface is grayish or mouse-colored and covered with a fine velvety pubescence.

Closely allied to these are the Japanese galls, which are so similar as to lead one to believe they are the same. They have, however, been assigned by Siebold to *Rhus Japonica* and by Murray to *Rhus javanica*. Being more deeply lobed than the Chinese variety, they are consequently more irregular in form.

Although the Japanese galls are preferred by some, the two varieties are usually employed indiscriminately. Large quantities of both under the name of Chinese

galls are used in Germany and the United States for the manufacture of tannic acid, of which they contain about 70 per cent. They were received in Europe as early as 1817, when they were analyzed by Brande, who stated that they yielded to cold distilled water 75 per cent., and to alcohol the residue gave an additional 4 per cent., leaving 21 per cent. of woody fibre.

It was not until 1844 that these galls were recognized to be of any value, so that our knowledge of their constituents dates from that time. The Japanese variety was first brought prominently to notice at the Paris Exposition in 1878.

W. Stein in 1849, under the name of a new kind of galls, described the Chinese variety as having the odor of tobacco and yielding 2 per cent. of ash, consisting of potassium, magnesium, calcium, and iron combined with phosphoric, silicic, and carbonic acids and chlorine. The other constituents were given as follows:

Tannic acid	69.00 per cent.
Other tannins	4.00 "
Saponifiable fat	1.00 "
Starch	8.00 "
Wood fibre	5.00 "
Inert material	13.00 "
	100.00 "

L. F. Bley in 1850 found that ether dissolved 76 per cent., that moisture amounted to 8 per cent., and that the ash was alkaline, nearly free from calcium salts, but rich in potassium and phosphoric acid. Büchner in 1851 stated that ether-alcohol extracted 74.35 per cent., while Leconnet obtained by maceration with ether 66.66 per cent.

Büchner considered the tannin identical with that of oak-bark. In comparison with the above he found that Aleppo galls gave to

Ether	77.00 per cent.	of extract.
Ether-alcohol	80.40 "	"
Cold water	86.50 "	"

Under the commercial name of "Chinese pear-galls," Hartwich in 1875 described a species of galls, which he found to contain 72 per cent. of tannin. He was unable to ascertain the botanical source, but they probably belonged to one of the above varieties.

A number of other varieties of galls have been analyzed and described from time to time; their use, however, has usually been confined to the locality in which they grow.

Among these may be mentioned the Bassorah, Burmah, or Mecca galls, which were analyzed by L. F. Bley in 1853, with the following results:

Tannic acid	26.00 per cent.
Gallic acid	1.60 "
Fatty oil	0.60 "
Resin	3.40 "
Extractive and salts	2.00 "
Starch	8.40 "
Woody fibre	46.00 "
Moisture	12.00 "
	100.00 "

They were described as reddish-brown in color, from the size of a hazel-nut to that of a small apple. They were believed to be produced on the *Quercus tinctoria* by the sting of *Cynips isana*, and by Lambert were

considered identical with the "Sodom Apple" of the ancient writers. They were used in the Orient in the process of dyeing Turkey red.

Piedmontese galls are developed on the acorns of *Quercus pedunculata*, *Quercus sessiliflora*, and some other species, by the sting of the *Cynips Quercus-calycis*. They are known as *knoppern* or *acorn-galls*. These galls, which are of the size of a hazel-nut to that of a walnut, are collected in the large forests of Austria-Hungary from August to October, and are brought into commerce partly whole, partly in the powdered condition, and are either used directly in one of these forms or are converted into extract. They contain about 45 per cent. of tannic acid, which, according to Löwe, is identical with that obtained from other galls. Some authorities give 20 per cent., others 50 per cent., as the tannin strength of these acorn-galls, and, no doubt, they vary greatly in value according to the time of collection. They are largely used by the tanners throughout Austria.

The German galls are produced on the twigs of *Quercus robur*, and are probably identical with the English galls analyzed by Watson Smith in 1869, with the following results:

Tannic acid	26.71 per cent.
Gallic acid	traces only.
Woody fibre	47.88 per cent.
Moisture	20.61 "
Coloring and loss	4.80 "
	100.00 "

They were obtained directly from Cheshire, and the author suggested that the absence of gallic acid was

due to their having been analyzed while in the fresh condition.

French galls, from *Quercus ilex*, are round, hard, light, reddish-brown, and related to the Burgundian galls from *Quercus cerris*, from which are also produced the Greek as well as the Italian galls. The commercial name of Trieste galls is usually applied to those from *Q. cerris*. Istrian galls are very small, light, pale yellow in color, and contain 24 per cent. of tannic acid. Hungarian galls, from *Q. Austriaca*, are characterized by being covered with wart-like protuberances.

Pistacia galls are produced on the plants of a genus of that name, belonging to the same natural order as the *Rhus*. Guibourt described one variety, produced on a plant of the genus *Terebinthus*, as a flattened vesicle enlarged in the middle and tapering to a point at each end, seven centimetres long and seventeen millimetres broad, with a very astringent taste and an odor resembling Chio turpentine. Another variety produced on the pistacia was described as from four to six centimetres in length and eight to fifteen millimetres in breadth, terminating by a sharp point. The taste was described as simply mucilaginous and aromatic without astringency.

Tamarisk galls were described by Holmes as of the size of a pea to that of a bean, and containing 40 per per cent. of tannic acid. Those from Morocco are produced on *Tamarix articulata*. In India similar galls are produced on *T. Gallica* and *T. orientalis*. They are much used by the natives medicinally.

Numerous varieties of galls have been noticed in the

United States, one from Texas on the *Q. virens*, or live-oak, is said to closely resemble Aleppo galls, and to contain 40 per cent. of tannic acid. Another variety, from California, formed on *Q. lobata*, is soft and spongy but very astringent.

Dr. Squibb in 1873 stated that American galls from oak and sumac have been found valuable sources for gallic acid.

In 1890 galls collected in the vicinity of Philadelphia by the author from the leaves of *Q. alba* in the month of July, and identified by Mr. L. O. Howard, entomologist of the United States Department of Agriculture, as having been produced by the insect *Acraspis erinacei*, were found to contain 17.89 per cent. of tannic acid. The moisture was found to be 45.95 per cent., and ash 0.60 per cent. These galls are found most abundantly on the young white oaks, and may be recognized by their covering of purple spines. Another variety collected in August from the twigs of the same oak, and identified by Mr. Howard as "a *Dipterous* gall made by some species of *Cecidomyia* or *Diplosis*," was found to contain as an average of three estimations 9.34 per cent. tannic acid, 73.19 per cent. of moisture, and 0.46 per cent. of ash. The same variety rapidly dried by artificial heat at about 80°, so as to destroy the insect, yielded 31.68 per cent. of tannin, 11.34 per cent. of moisture, and 2.6 per cent. of ash. Another variety, also collected in August, from the leaves of *Q. palustris*, and stated by Mr. Howard to have been produced by *Holcarpis globulus*, Fitch, gave 3.91 per cent. tannic acid, 58.73 per cent. moisture, and 0.77 per cent. ash.

An unidentified variety, collected from the leaves of *Rhus glabra*, and in many respects the counterpart of the Chinese galls, was allowed to become air-dried, and then found to contain 61.70 per cent. of tannic acid, 12.93 per cent. of moisture, and 2.04 per cent. of ash. Some previous experience has shown that the white-oak galls if allowed to become air-dried lose their tannic acid, presumably by the development of the insect, so that, to determine the tannin value, either the galls in the moist state must be employed, or they must be subjected to sufficient artificial heat to destroy the insect.

SECTION II.

HISTORY.

WHILE the general history in a preceding section refers largely to this member of the class, it is found necessary now to treat the history of each tannin separately, beginning with 1802, when Proust made the statement that there were many different kinds of tannin.

Davy published in 1803 the results of two years' labor on the subject, which was prefaced by some historical remarks, in which he, like Karsten, attributed the discovery of tannin to Seguin, although he called attention to the fact that Dizé first noticed the precipitate caused by the addition of sulphuric acid to infusion of galls. He further reviewed the work of Deyeux and Proust, giving the former much credit for his "able memoir," but to the claim of the latter, "that there exist different species of the tanning principle, possessed of different properties and different powers of acting upon reagents, but all precipitable by gelatin," he answered, that, while probable, it could "not be considered settled until the tannin in the different vegetables has been examined in its pure and isolated state." He did not accept all of Seguin's theories about the action of infusion of galls on animal membrane, and considered them unwarranted by facts.

Thus far the papers quoted confined themselves to

the history and discovery of tannin; therefore it is not surprising that in 1804 we find a contribution by Trommsdorff on the nature of this astringent principle in galls. His investigations somewhat resembled those of Deyeux. The work was divided into fifty-five experiments, in which he studied the precipitates caused by hydrochloric and sulphuric acids on infusion of galls, and added the observation that acetic and phosphoric acids likewise caused precipitates with tannin, while oxalic, tartaric, and malic acids caused no precipitates. He noticed the effect of tannin solution, after removal of gallic acid, on litmus-paper, and further endeavored to obtain pure tannin by Proust's method of precipitation with potassium bicarbonate, but found much tannin in the filtrate, and finally concluded that the precipitate contained calcium and that Proust erred in his new method. The same conclusions were reached in regard to Proust's other methods by precipitation with mineral acids. This long, and at that time valuable, series of experiments was abruptly terminated without drawing conclusions, as he hoped to continue his investigations.

After the above communication no important results are recorded until Sertürner, an apothecary in Eimbeck, during the year 1812, published his experiments, in which he established the absence of nitrogen, and made some observations on the action of alkalies on tannin, and the change into gallic acid. As, however, his results were in part a repetition of those obtained by previous investigators, his work was not kindly criticised by Gehlen.

While there were a number of contributions on this

subject from year to year, nothing stands out prominently until the work of Berzelius in 1827, which appeared in the *Jahresbericht* and in his text-book. After remarking that every investigator offered a new method of preparation, he proposed two of his own, one by precipitating a clear infusion of nutgalls with sulphuric acid, and the other by a similar precipitation with potassium carbonate. At that time there was no distinction between the tannin of the nutgall and that from the oak-bark, since both are described as "Eichen-Gerbstoff," and further he stated that the "entire oak genus contains a tannin which appears to be identical." The change of tannin into gallic acid had not been fully investigated at that time; Berzelius observed that the question is whether gallic acid is formed by the destruction of tannin, or whether it results from the setting free of a substance with which it was in combination. He used the classification depending on the color with iron salts, and described as giving a blue color the oak, sumac, alder, birch, and a few others, and as producing a green color that of cinchona, catechu, kino, fir, and pine. He also reported what was probably the first determination of the ultimate composition of tannin. The lead salt was used, and his conclusion was that $C_{18}H_{18}O_{12}$ most nearly represented the formula of tannin.

This work of Berzelius is full of historical data, and many of his results are as true to-day as at that time. He gave the credit of discovery to Deyeux in the following language: "The operation of tanning was known to the ancients, but the substance which combined with the hide was first noticed by Deyeux, and

afterwards with more exactness investigated by Seguin. Proust endeavored to discover a method of separation."

In 1832, Geiger, by a series of investigations on tannin and the action of that substance on iron salts, came to the following conclusions: (1) All tannins are identical, (2) the iron-green tannins become iron-black if the free acid present be neutralized by an alkali or by iron, and (3) the iron-black tannins by the addition of some acid, especially tartaric, become iron-green. Berzelius, however, did not accept this, and he stated in his *Jahresbericht* that he too had noticed this peculiarity of the tannins with iron salts under different circumstances, but attributed it to a play of colors, since by standing a black precipitate separated.

In Buchner's *Repertorium für die Pharmacie*, **46**, 316, 1833, we find a review of a prize essay by A. W. Buchner on the subject of "The most Recent Discoveries on Tannic Acid or the so-called Tannin (Gerbstoff)." This was written in answer to the following questions, offered in 1824 by the Harlem Royal Academy of Natural Sciences:

"Is the so-called tannin, which we extract from different plants, a true principle, or have we given this name to different plant principles which possess the general properties of astringency and of forming leather?

"By what means can we best extract these substances from the various plants in a state of purity, and how determine that they are unmixed and distinct?

"Which is the best and most ready method for preparing tanning materials from the charcoal of indigo and other vegetable substances with acid, and how

far is this artificially prepared tannin distinguishable from the natural? Are not the two identical substances?

"In case of arriving at a fuller knowledge of the different tanning substances, to what use are the various ones best adapted in tanning and manufacturing as well as in medicine?"

While the answers to these questions are full of interest, it is impossible to see that the knowledge of the subject was very materially advanced by the writer. Some of the questions are still unsolved.

The next important work was in 1834, when a memoir was presented to the Institute of France by Pelouze, which memoir was widely copied and appears to have caused a general awakening among the scientists of that day to a closer investigation of this almost dormant subject.

Probably the most important part of Pelouze's memoir was the new method proposed for preparing tannin. This process is the one usually quoted in the textbooks at the present day, and is well adapted for the extraction of the tannin from a substance as rich in it as nutgalls.

Briefly, it consists in extracting galls with ether containing some alcohol and water. The solution separates into two layers, the upper an ethereal one of gallic acid with some tannin, the lower an aqueous solution of tannin containing some ether. This aqueous solution on evaporation leaves a porous mass of tannin, which Pelouze claimed was quite pure.

This substance gave on drying at 120° the following percentage composition:

	I.	II.	III.	IV.
C	51.77	51.56	51.20	51.72
H	3.98	4.37	4.29	4.17
O	44.25	44.07	44.51	44.11
	100.00	100.00	100.00	100.00

These figures, he stated, closely agreed with those obtained by Berzelius and indicated the formula $C_{18}H_{18}O_{12}$.

The remainder of the memoir was devoted to showing the acid properties of the tannin and its capability to form definite salts with the different bases. He further stated that gallic acid did not pre-exist in the galls, but that it was a product of atmospheric action on tannin, that at a temperature of 215° it was transformed into pyrogallic acid and carbon dioxide, and that pyrogallic acid in turn was converted into metagallic acid and water. This appears to have been the first statement, based on experiment, that tannin becomes converted into gallic acid through the influence of atmospheric oxygen.

This work of Pelouze attracted general attention to the subject, and in the same year Liebig published his results on an elementary analysis in which he found:

C	52.50
H	4.12
O	43.38
	100.00

and concluded that $C_{18}H_{16}O_{12}$ more closely represented the formula. This he communicated to Pelouze, who undertook anew the analysis, obtaining the following percentage composition:

	I.	II.
C	51.30	51.86
H	3.83	3.76
O	44.87	44.88
	100.00	100.00

These results he shortly after sent in a letter to Liebig, in which he stated that, while the difference was very slight, he was inclined to accept the latter's formula of $C_{18}H_{16}O_{12}$, in which view Dumas concurred. With some unimportant reservations Berzelius, in his *Jahresbericht*, 1840, accepted this formula also.

In 1836, Leconnet suggested another method for preparing tannin, by stirring finely-powdered galls with sufficient ether to make a thin mixture, and allowing to stand twenty-four hours. The mass was then pressed between strong linen, this process was repeated with more ether, and the syrupy liquid evaporated. He claimed a larger yield (40 to 60 per cent.) than that obtained by Pelouze, with the use of much less ether.

Robiquet about this time directed his attention to the decomposition of tannin with the formation of gallic acid. Contrary to the observations of Pelouze, he found that the change to gallic acid would take place without access of air or oxygen, but found it was caused by a ferment in the galls. These observations were confirmed by Larocque in 1841.

Previous to the investigations of Stenhouse in 1842, such authorities as Pelouze, Berzelius, and Liebig considered the tannins from all sources to be identical, differing only in purity. Although Proust had stated forty years before that there probably existed "several different species of the tanning principle," Stenhouse

was the first to prove this by experiment. In all the writings to this time the term "gallotannic acid" was applied to that from oak bark or wood as well as that from galls. Stenhouse, by adopting a method used at the present time to study the tannins,—namely, by heating to decomposition,—found the oak-bark tannin yielded no pyrogallol. The only substance yielding true gallotannic acid was found to be sumac, and this, so far as the sumac is concerned, has never been disproved. He also showed by experiment that there was a distinction between the tannins which produced a blue and those which produced a green precipitate with iron salts, thereby contradicting several previous investigators, as well as the expressed opinion of Berzelius. The subject of iron-bluing and iron-greening tannins attracted considerable attention about this time, and several other chemists devoted their energies to solving the problem of classification by this means, but with indifferent success.

The work of Dominé in 1844 has been very extensively quoted, because he offered some improvements on the method of Leconnet for preparing tannin. He claimed that alcohol was an unnecessary constituent of the ether used in extracting galls, but that the presence of a small quantity of water was very essential. The method proposed was to allow the galls to become saturated with the damp atmosphere of a cellar by exposure of some days, then mix with sufficient ether to make a paste, and express, this expression to be repeated with ether which had been shaken with six per cent. of water. This process was at one time adopted by both the United States and British Pharmacopœias.

From this time those who worked with tannin busied themselves with attempting to arrive at its constitution as well as its composition; Liebig's formula, $C_{18}H_{16}O_{12}$, did not convey a sufficiently satisfactory idea of what relation tannin bore to other allied compounds, especially to gallic and pyrogallic acids.

A few investigators stand out prominently. Of these Wetherill first carefully investigated the conversion of tannic into gallic acid, by boiling 50 grammes of tannic acid with 500 cc. of a solution made by mixing one volume of sulphuric acid, specific gravity 1.840, with four volumes of water. He obtained from 100 parts of tannic acid 87.4 parts of gallic acid.

About the same time, 1847, Mulder made a valuable contribution on the subject. The original being in Dutch and in a publication not found in this country, a full translation may be found in Buchner's *Repertorium für die Pharmacie*, **101**, 311, and Erdmann's and Marchand's *Journal*, **17**, 337. Berzelius, *Jahresbericht*, 1850, 224, gave a short abstract of it, and appended some critical remarks of his own, which indicated that he did not believe this work of Mulder in any way superior to the great number of other publications on the subject.

Mulder stated in the introductory remarks that the formula of Liebig had been generally accepted, but that he found it to be $C_{28}H_{18}O_{17} + H_2O$, which compactly stated in our nomenclature is $C_{14}H_{10}O_9$, or exactly that which has been established by more recent investigators and is accepted at the present time. This determination was made on tannic acid which had been dried at 120°. He gave much credit to Pelouze, and stated that

no better method of preparing the acid had since been discovered.

After further reviewing the work of Pelouze on pyrogallic and melangallic (metagallic) acids, he studied the conversion of tannic into gallic acid by the action of other acids; the action of alkalies on tannic, gallic, and ellagic acids; the percentage composition of tannic acid and its formula; the action of ammonia; and, finally, some of the tannates, especially of lead.

With the exception of the work done by Liebig, it is safe to say that this work of Mulder was the most elaborate investigation after that of Pelouze, which in many respects it resembled.

While there were about the year 1850 a number of creditable publications, nothing is of great historical value until we reach the work of Strecker in 1852 and 1854, which he carried out in Liebig's laboratory. These contributions are among the few that stand out prominently, for, besides reviewing some of the work of others, he detected the presence of sugar, as had been previously indicated in Liebig's revision of Geiger's *Handbuch der Pharmacie*, edition of 1843, page 854, where it is stated that Braconnot found in the fermentation of galls alcohol and carbon dioxide, which indicated the presence of sugar, that had not been previously noted, and that tannic acid contained "the elements of six atoms of gallic acid and one atom of grape-sugar." Strecker had noticed that by heating tannic acid carefully a large carbon residue was obtained, when it had been previously supposed that the only decomposition products were pyrogallic acid and carbon dioxide. He also obtained the reactions for

sugar in the solution remaining after converting tannic into gallic acid, by treating this solution with acetate of lead, filtering, removing the lead from the filtrate by hydrogen sulphide, and applying potassium hydrate and copper sulphate, whereby he obtained the reduction to cuprous oxide. This he attributed to the presence of sugar or a related carbohydrate. He further investigated the elementary composition of tannic acid and arrived at the formula $C_{40}H_{36}O_{26}$, and he explained the change into gallic acid and sugar as follows:

$$C_{40}H_{36}O_{26} + 10H_2O = 2C_{14}H_{16}O_{12} + C_{12}H_{24}O_{12}.$$

These formulas were changed somewhat in his second paper, two years later, when he arrived at the following conclusions:

"Tannic acid is a glucoside, and is split, through the action of acids, alkalies, or ferments, into gallic acid and glucose.

"The formula for tannic acid is $C_{54}H_{44}O_{34}$, in which three equivalents of water are replaced by metallic oxides. The precipitate obtained by acting on tannic acid solution with acetate of lead consists in great part of a basic salt in which are contained ten equivalents of lead oxide to one equivalent of tannic acid.

"The hitherto accepted compounds of tannic acid with hydrochloric and sulphuric acids do not exist.

"Gallic acid, $C_{14}H_{12}O_{10}$, is, as tannic acid, a dibasic acid.

"Other tannins are likewise glucosides, and contain apparently also thirty-four equivalents of oxygen."

The tannic acid used in these experiments was prepared by Pelouze's method, and purified in one case by

dissolving in water and precipitating with ether, and in another case by dissolving in ether and precipitating with water. By these operations different layers were obtained, the heaviest of which he considered the purest and separated. These were then evaporated *in vacuo* and heated to 125°. Seven different preparations gave, when burned with copper oxide, closely agreeing results. He offered, as further evidence of the glucosidal nature of the acid, the fact that *Wetherill* obtained 87 *per cent. of gallic acid* and *he* found 22 *per cent. of glucose.*

Robiquet in 1852 arrived at somewhat different conclusions, but these were not backed by such a mass of experimental data as characterized Strecker's.

The work of Strecker might be a fitting close to the historical consideration, since the next important work brings us to such a modern period that it may be more properly studied under the properties and constitution of the acid.

The authors, however, should be mentioned in this connection; therefore we must give to Julius Löwe and Hugo Schiff the credit of independently establishing by careful research our present knowledge of tannic acid. The former in 1867 first succeeded in reconverting gallic into tannic acid by treating barium gallate with silver nitrate and obtaining a substance which he described as precipitating gelatin and the alkaloids. His work was taken up by Schiff in 1871 and carried on for several years, and to this latter scientist we owe our present knowledge of digallic acid. It is worthy of note, however, as has been already stated, that most discoveries are in a certain degree anticipated, and this one of digallic acid was no exception, for Hlasiwetz in

1867 announced that, "If tannin is not a glucoside, it may perhaps be a digallic acid. The analyses of tannin and its salts agree with this composition as well as can be expected in the case of a substance which is so difficult to purify."

Löwe in 1872 contributed a paper on pure gallotannic acid, in which he described a method of purification by acetic ether, which will be more fully considered under the appropriate head.

Notwithstanding the fact that most chemists at the present time devote themselves to the study of what may be termed artificial products, still those who have contributed to the literature of tannic acid during the last score of years could not be so much as mentioned in this brief history. During the past decade much time and earnest labor have been given to the endeavor to discover a universal method of estimating not only tannic acid but all tannins, and it is the intention that each author shall receive his full share of credit in the other parts of this work.

SECTION III.

THE PREPARATION AND PURIFICATION OF TANNIC ACID.

THE separation of tannic acid in a nearly pure state was first accomplished by Proust in 1798, by precipitating the infusion of galls with stannous chloride, separating the tin from the precipitate by hydrogen sulphide, and evaporating the filtrate to dryness. This method, with its variation by using lead acetate in place of the tin salt, has done good service. The same in a lesser degree may be said of the process proposed by Berzelius, which consisted in precipitating the tannic acid by sulphuric or hydrochloric acid, digesting the precipitate, of tannic acid with the acid used, with lead carbonate, filtering, and evaporating to dryness. The above methods are not available for producing the acid on a large scale; and that by precipitation with hydrochloric or sulphuric acid is applicable only to galls.

The numerous processes for obtaining tannic acid from galls became practically valueless after Pelouze in 1834 published his method for obtaining the acid by percolating galls with ether. This method, which is the one usually quoted in the text-books, consists in percolating powdered galls with commercial ether containing alcohol and water.

The details of the operation are to pack the powder

in a cylindrical percolator, the upper end of which is narrow in order that it may be stopped to prevent the evaporation of the solvent. The lower end of the percolator is plugged with cotton and connected with a flask, ether is poured on the powder, and the ethereal solution of the galls allowed to collect. This solution soon separates into two layers, the upper of which consists of ether, gallic and ellagic acids, resin, and fat, with some tannic acid, while the lower is a solution of moderately pure tannic acid in water and ether. The percolation is discontinued when the lower layer ceases to increase in volume. The two layers are then separated, and the lower one evaporated to dryness on a water-bath, by which means the acid is obtained in a porous mass.

There have been, since the publication of this process, numerous modifications of it suggested, but the principle remains the same. The product is not absolutely pure tannic acid, but a mixture of that compound with gallic acid, coloring-matter, resin, and glucose. It is, however, a process that is adapted to working with large quantities, where there are facilities for recovering the ether.

In order to obviate using so much ether, many methods have been offered as superior to the above, notably one by extracting with water and precipitating with lead acetate. It is, however, a wasteful process and is difficult and tedious to perform.

Mixtures of alcohol, ether, and water in various proportions have been suggested for percolating galls, instead of the commercial ether alone. Four parts of ether and one part of alcohol have been recommended as the most suitable solvent, although thirty parts ether

(specific gravity 0.740), four parts water, and one part alcohol (90 per cent.) also make a good solvent. Equally good is the United States Pharmacopœia ether (specific gravity 0.750), which is composed of seventy-four parts ether and twenty-six parts alcohol with a little water. Equal volumes of ether and alcohol have been recommended on account of the increased yield obtained; the product, however, is not so pure as that from a more ethereal solvent.

In 1836, Leconnet proposed a method for extracting tannic acid by mixing the powdered galls with sufficient ether to make a paste, allowing the mixture to macerate, then expressing through muslin, and repeating the process with more ether. The yield was found to be 60 per cent., and a comparatively small quantity of ether was employed.

The process as modified by Dominé in 1844 was adopted by the British and United States Pharmacopœias. This modification consisted in first exposing the powdered galls in a damp cellar for several days, to allow the absorption of moisture, and then macerating with commercial ether and expressing as in Leconnet's process.

It has further been suggested to extract galls in such a manner as to form three layers of the percolate. To accomplish this, 10 parts of coarsely-powdered galls are placed in a percolator and a mixture of 12 parts stronger ether and 3 parts alcohol poured on, and the mixture allowed to stand two days, when the percolation is commenced and continued with the same mixture of ether and alcohol until 10 parts are obtained. The resulting percolate is mixed with one-third its

volume of water, agitated well, and allowed to stand, when it will be found that three layers have formed. The under, watery layer contains nearly pure tannic acid, and is evaporated rapidly in a vacuum, which causes the acid to become porous. The upper layers are distilled to recover the ether-alcohol, and from the residue water extracts a small quantity of impure tannin. The last method can be recommended only where it is desired to obtain a pure acid without the trouble of additional purification, for if made from Chinese galls the product should be as pure as it is possible to get the acid in one operation. It is not available as a commercial process, on account of its expensiveness, since the quantity of solvent recommended is insufficient to completely extract the galls.

The above-mentioned processes have been enumerated in order to criticise them, and at the same time furnish information to those who wish to prepare tannic acid from galls on a small scale. The following will treat the subject from a commercial stand-point, and describe what has been a process for producing the tannic acid in quantity.

There are three varieties of the acid in commerce, known as—

Ether-tannin (the German Schaum-Tannin),
Alcohol-tannin,
Water-tannin.

The first is the one best known in this country, although one or both of the others may be had of importers and manufacturers under the name of "commercial tannin."

The Chinese or Japanese galls, on account of their greater freedom from coloring-matter and larger per-

centage of tannic acid, are by the manufacturer preferred to the Turkish variety.

The galls are first crushed and then passed through a mill which will powder by cutting rather than by grinding, so as to furnish a moderately fine powder that is not "balled" or "caked."

A quantity of the powder is then stirred, in a wooden or copper vessel, with sufficient water to form a concentrated aqueous solution, or this may better be accomplished with a more complete exhaustion of the galls by a battery of vessels or extractors in which the liquors are run from one to another until of proper strength. The temperature of the water is recommended to be from 40° to 60°, although this varies with different manufacturers. When the liquors have reached the proper strength, they are run into a large settling-vessel and allowed to cool and settle for twelve hours; especially is this necessary if a higher temperature than that above mentioned has been used. From the settling-tub the liquor is run through a filter into a cylindrical copper vessel like a churn, in which are numerous paddles so attached as to be capable of slow and continuous revolution. To the liquor in this vessel about one-fourth its volume of ether (specific gravity .750) is added. The mixture is then thoroughly agitated by means of paddles. The longer this operation is continued the better the product is supposed to be, and when completed the emulsion-like liquid is run into a settling-vessel and allowed to stand for from eight to ten days, at the end of which time the complete separation into two layers will be found to have taken place.

The upper, ethereal layer, which holds in solution

resin, fat, coloring-matter, gallic and ellagic acids, is drawn off and the ether recovered by distillation. The lower layer, consisting of water, ether, tannic acid, and some impurities, is also run into a still and a portion of the ether recovered by distillation until the liquid reaches a syrupy consistence. After cooling, this liquid, which still contains some ether, is spread by means of a brush on plates of sheet tin, and the tin plates are placed for a moment on the hot steam-coil, or flat iron surface heated with steam, and over the whole is placed a wooden box. The tannic acid almost immediately "puffs up" and dries, although this spongy condition is said to be materially assisted by passing over the acid a jet of dry steam, which softens it slightly and admits of its swelling still further. Considerable practice and dexterity are required in this operation, which exposes the operator to the vapor of ether unless great precautions are taken. Excellent results have also been gotten by spreading the solution on plates of glass and placing them in a drying-oven heated to 110°, which may be so ventilated as to protect the operator.

The product is the ether-tannin, and should be nearly white and completely soluble in water and in alcohol.

The needle or so-called "crystal-tannin" is prepared as above, but, instead of spreading the solution on tin or glass, it is run through small holes and allowed to fall in a very thin stream on a revolving hot cylinder of copper, from which the dried product is scraped in the needle form, which gives the impression of its being crystallized.

Alcohol-tannin is prepared by extracting the galls with diluted alcohol (50 per cent.) instead of water, care-

fully filtering, recovering as much of the alcohol as possible, and completing the evaporation in a vacuum. It is then broken into pieces which resemble rosin, and sent into commerce in that form, or it is first powdered by porcelain rollers, which operation gives it a much lighter color. The product should be completely soluble in water, indicating its freedom from resin.

Water-tannin is extracted similarly to the ether-tannin, but after filtering, instead of mixing with ether, the solution is run directly into a vacuum-pan and concentrated to dryness. It usually comes in commerce in the powdered form, which operation is accomplished similarly to the alcohol-tannin.

Purification.—Tannic acid prepared by the foregoing methods is contaminated with fat, wax, resin, coloring-matter, gallic acid, and glucose. For most purposes the small amounts of these impurities are no objection, but at times the chemist desires a product free from more than traces of impurity, especially when the object is to determine its ultimate composition. The fat, wax, some coloring-matter, and the odorous principle may be removed by percolation with petroleum ether.

A number of processes have been suggested for removing the other impurities, all of which, however, are attended with considerable waste. One method is to take the best ether-tannin and treat it with stronger ether, to which just sufficient water is added to effect solution. This is best accomplished by using 100 grammes of the tannic acid, 150 cc. of stronger ether, and 100 cc. of water. Three layers are formed, the lowest of which is a concentrated solution of nearly pure tannic acid. Considerable loss occurs by this pro-

cess, as the middle layer contains some of the acid, which, however, may be recovered by distilling the ether and water under reduced pressure. The upper layer consists of ether holding in solution resin, coloring-matter, and gallic acid.

Another method of purification consists in dissolving the acid in water almost to saturation, and allowing to stand to separate the resin and other insoluble impurities. The clear liquid is removed by decantation, and there is added to it a clear saturated solution of common salt, to this is added some solid sodium chloride in order to completely precipitate the acid, which is collected on a filter, dried carefully, and dissolved in a mixture of alcohol and ether, or in acetic ether. Löwe recommended to agitate the mixture after addition of salt with acetic ether. In either case the solvent is recovered by distillation, the residue dissolved in water and agitated with ether, the latter separated, and the aqueous solution distilled on a water-bath to dryness under reduced pressure, which causes the acid to become light colored and porous. Glucose is the most tenacious impurity, resulting in part from the decomposition of the tannic acid during each purification.

The following process, a combination of some previously-proposed methods, has been used by the author with complete success, although, like other processes, it is attended with considerable loss, which, however, might in part be obviated if the quantity desired were sufficient to warrant it.

Ten grammes of tannic acid are dissolved in 200 cc. of water, and to the unfiltered solution a 10-per-cent. solution of lead acetate is added drop by drop with con-

stant stirring until the precipitate ceases to be granular, but is more milky in character, ceases to settle, and is pure white in color, distinct from the yellowish color caused by the first drops of the reagent. The filtrate at this point will be colorless. It is important that the solutions be as dilute as the above mentioned, or else the precipitate of lead tannate will not carry down the coloring-matter with it. After filtration the precipitate is washed with sufficient water to bring the filtrate to the original volume. More washing than this is to be avoided, on account of the tendency of the precipitate to decompose.

The colorless filtrate, which contains free acetic acid, is agitated with 75 cc. of pure acetic ether and the latter separated; this agitation is to be repeated twice with the same volume of acetic ether; the three portions are mixed and the ether recovered by distillation under reduced pressure to dryness. A light, porous, white tannic acid is obtained amounting to 41 per cent. of the original quantity. It contains gallic acid and has a pungent acetous odor; the aqueous solution of a portion of it, after the removal of the tannic acid by lead oxyacetate, gives no reaction with Fehling's solution for glucose. The tannic acid is further purified by dissolving in water, agitating the solution with stronger ether to remove gallic acid, and distilling the aqueous solution to dryness under reduced pressure. This is once more dissolved in ether with a little water, and again brought rapidly to dryness under reduced pressure. The result is a pure white product which gives no reactions for gallic acid or glucose. A sample pre-

pared by these directions when dried at 120° gave the following percentage composition :

C	52.10	per cent.
H	3.52	"
O	44.38	"
	100.00	"

An acetyl derivative was prepared of the same sample which melted at 139°, and by boiling with magnesium oxide according to the usual process gave very close to the theoretical quantity of magnesium pyrophosphate that would indicate pentacetyl-tannin.

SECTION IV.

THE PROPERTIES OF TANNIC ACID.

TANNIC ACID occurs in yellowish-white amorphous powder or masses which are easily pulverized; it is odorless, and possesses a strongly astringent taste, free from bitterness. By exposure to light it becomes yellow to brown in color.

It is soluble in 6 parts of water, in 6 parts of glycerin, and in 0.6 part of alcohol. The solutions are yellow in color, react acid with litmus, and are nearly without action on polarized light. Ether containing water or alcohol dissolves tannic acid, but absolute ether dissolves it sparingly, while it is insoluble in chloroform, benzol, petroleum ether, carbon disulphide, fixed and volatile oils, except oil of bitter almond, which dissolves it.

A number of salts, as potassium acetate, ammonium chloride, calcium chloride, and sodium chloride, as well as the mineral acids, sulphuric, hydrochloric, arsenic, and boric acids, precipitate tannic acid from its concentrated aqueous solution. Nitric acid does not so precipitate it. When air and light are excluded from the aqueous solution of tannic acid, it remains for some time without decomposition, but in contact with air oxygen is absorbed, with the formation of a dark color and the production of sugar, gallic acid, and sometimes

ellagic acid; by prolonging this action carbon dioxide and oxalic acid also result.

When subjected to heat tannic acid changes but little until 120° is reached, when it assumes a grayish color, without, however, undergoing apparent decomposition, at 140° it is darker, and at from 160° to 215° there are formed carbon dioxide, pyrogallic acid, water, and metagallic acid. The last is not volatile, while the others are volatile; and this admits of a ready method of separating the meta-acid, which remains behind as a black, amorphous mass, from the pyro-acid, which sublimes in acicular crystals. Since the latter volatilizes at 210°, it is natural to suppose that, in order to obtain it from tannic acid, its volatilizing temperature must be reached; but it is found that the decomposition begins at 160°, and, in the escape of carbon dioxide and water, pyrogallic acid is carried off and condensed in the cooler parts of the vessel. The best yield is obtained by allowing the temperature to rise very slowly to 215°, keeping it between 190° and 210° for one-half hour. If the heat be increased rapidly to 215°, there will be a small quantity of the pyro-acid and a larger amount of the meta-acid produced.

On heating with a 2-per-cent. solution of absolute hydrochloric acid, tannic acid is converted into gallic acid:

$$C_{14}H_{10}O_9 + H_2O = 2C_7H_6O_5.$$

The pure acid yields gallic acid only, but that usually met with gives variable amounts of glucose and ellagic acid at the same time.

With solutions of the alkalies gallic acid is formed,

together with a dark color due in part to metagallic acid and in part, when commercial acid is used, to the action of the alkali on the glucose present.

Ammonia acts differently from the fixed alkalies. When tannic acid is heated with aqueous ammonia in an atmosphere free from oxygen, which is best accomplished by passing hydrogen into the mixture, there are formed gallamide and ammonium gallate, according to the following equation:

$$C_{14}H_{10}O_9 + 2NH_3 = C_7H_5O_4NH_2 + NH_4C_7H_5O_5.$$

Fermentation causes the change of tannic into gallic acid, several decomposition products resulting at the same time.

Ferric salts produce a blue-black color or precipitate with tannic acid, according to the concentration of the solutions. When the solution of iron salt is very dilute, or when free acid, especially tartaric, is present, the color is greenish.

Ferrous salts, when perfectly pure, added to tannic acid solution produce no change unless the solutions be concentrated, when a white gelatinous precipitate forms. The least trace of ferric salt is sufficient to change this to a dark-blue color or precipitate, according to the strength of the solution. Soluble vanadium salts also produce the blue-black color or precipitate with tannic acid.

Tannic acid precipitates most alkaloids and bitter principles. It gives a light-colored flocculent precipitate with gelatin, which is rendered more insoluble by alum, ammonium chloride, or sodium chloride; solutions of starch and albumen are similarly precipitated.

Most metallic salts form precipitates with tannic acid: tin salts produce a light-colored precipitate; lead salts, a white precipitate, which darkens on exposure to air; copper salts give a dark-brown precipitate; and silver salts, brown precipitates. Tartar emetic causes no precipitate until ammonium chloride is added. Manganese acetate causes a white precipitate; uranium acetate, a crimson or dark-red color, changing to a brown precipitate; potassium dichromate gives a brown precipitate; lime-water causes a white precipitate, turning blue.

According to Berzelius, when boric acid is dissolved in a hot solution of tannic acid, there is formed a white jelly on cooling, which may be dried to a white powder. Tannic acid displaces carbon dioxide from carbonates and forms tannates; those of the alkalies rapidly turn dark when exposed to the air. Fehling's solution is reduced by tannic acid, with formation of cuprous oxide; in order, therefore, to determine the presence of glucose the acid must first be removed by lead acetate. A. H. Allen gives the following characteristic test for tannic acid: a dilute ammoniacal solution of potassium ferricyanide, which causes a deep-red color changing to brown. The reaction is very delicate, and the color is destroyed by an excess of the reagent. A similar reaction is caused by gallic acid.

Ammonium molybdate gives with tannic acid a reddish-yellow color, which is destroyed by oxalic acid. A solution of iodine in potassium iodide, when mixed with a small quantity of ammonia which has been previously diluted with ten times its volume of water, produces with tannic acid a brilliant red color.

Tannates are formed by addition of the acid to carbonates or hydrates in the case of the alkalies, and to hydrates in the case of the alkaline earths. With the metals it forms tannates on its addition to an acetate. By certain precautions the purity of the salt may be improved,—for instance, by the use of alcoholic solutions in the preparation of the alkali salts. Sodium tannate, $NaC_{14}H_9O_9$, and potassium tannate, $KC_{14}H_9O_9$, are obtained as crystalline precipitates by adding an alcoholic solution of the hydrate to an alcoholic solution of tannic acid; the precipitate dries to a fine powder.

Barium tannate, $Ba(C_{14}H_9O_9)_2$, is formed by precipitating the sodium salt with barium chloride. Another barium salt, of the formula $Ba(OH)C_{14}H_9O_9$, is formed by adding barium carbonate to a hot aqueous solution of tannic acid.

At least three lead salts are known. According to Pelouze and Strecker, the compound $3PbC_{14}H_8O_9 + Pb(C_{14}H_9O_9)_2 + 2H_2O$ is formed by precipitating lead acetate with an excess of tannic acid. Strecker is also authority for the compound $2PbC_{14}H_8O_9 + Pb(OH)_2$ by precipitating tannic acid with an excess of lead acetate, and the compound $Pb_3(C_{14}H_7O_9)_2 + 2Pb(OH)_2$ by heating an excess of lead acetate with a dilute tannic acid solution. Schiff found two salts according as the tannic acid or lead acetate is in excess, an excess of the acid giving $Pb_2C_{14}H_6O_9 + 2H_2O$ and an excess of the lead salt giving $Pb_3C_{14}H_4O_9$. The compounds with lead have probably been studied more than any of the other tannates, and many besides those given above have been described.

The tannates of iron have also received a large share

of attention. The compounds $Fe(C_{14}H_8O_9)(C_{14}H_9O_9)$ and $Fe(C_{14}H_9O_9)_3 + FeO(C_{14}H_9O_9)$ have been described. All the tannates of iron are unstable, and we know them best in solution as ink. A compound of tannic acid with aluminium has been prepared by adding aluminium hydrate to tannic acid solution; the compound is soluble in excess of the acid. Zinc tannate is formed by precipitating an alkali tannate with zinc sulphate, or by adding the acid to ammoniacal zinc sulphate. Copper tannate, $Cu_3C_{14}H_4O_9$, is formed by precipitating the acid with copper acetate. When alkali is added the precipitate redissolves, and reduction to cuprous oxide takes place. Wackenroder is authority for the statement that, when the copper tannate which has been prepared by an excess of the acid is dissolved in ammonium hydrate, the copper is not precipitated therefrom on the addition of hydrogen sulphide.

Compounds of tannic acid with nearly every known metal are described in many of the text-books, but many of these salts were made by the older chemists before the acid had been prepared pure; consequently, beyond the fact that we get insoluble compounds of a certain color, there is very little accurate knowledge concerning them.

SECTION V.

THE COMPOSITION AND CONSTITUTION OF TANNIC ACID.

As stated in the history, numerous investigators in the first half of this century made efforts to establish the composition of tannic acid. Mulder actually determined the formula, $C_{14}H_{10}O_9$, accepted at the present time. It was not, however, until Löwe in 1867 prepared digallic acid by treating barium gallate with silver nitrate, and Schiff in 1871 studied the conversion of gallic into tannic acid by means of phosphorus oxychloride, that the foundation of our present knowledge was laid.

No better idea can be given of the importance of Schiff's work than by quoting portions of his papers. He first called attention to the fact that some chemists held the view that tannic acid was a glucoside, while others considered glucose to be an admixture, which varied much in its proportion, and that the behavior of the acid towards reagents was not altered by the removal of the glucose. Schiff's method of forming digallic acid was as follows:

"When well-purified gallic acid dried at 110° is mixed with phosphorus oxychloride to the consistence of an emulsion and heated in a water-bath at 100° and afterwards in an oil-bath to 120°, there follows an abun-

dant evolution of hydrochloric acid. The gallic acid is converted into a yellow powder, which is washed by decantation with several portions of absolute ether.

"The ether is removed from the residue by gentle warming and then dissolved in a small quantity of water. After twelve hours' standing the gallic acid crystallizes out and is removed, and to the yellowish-red solution is added sufficient common salt to saturate it, causing a separation of the resin-like mass, which is easily separated from the liquid and washed twice with saturated salt solution.

"The resin-like mass is dried under reduced pressure, dissolved in a small quantity of absolute alcohol, to remove salt, and to the clear alcoholic solution is added an equal volume of ether, filtered, the solvent distilled off, and the amorphous residue dried in a vacuum.

"The varnish-like, nearly colorless residue gives *similar reactions, solubility, physical properties, taste, etc.*, which are considered characteristic of tannic acid.

"*It is the first absolutely sugar-free tannic acid.*"

The amorphous residue was entirely reconverted into gallic acid on boiling with hydrochloric acid, and this gallic acid again converted into the amorphous acid by the phosphorus oxychloride.

Two elementary analyses gave the following:

	I.	II.
C	51.7	52.3
H	3.8	4.1

The question in regard to the nature of tannic acid was answered as follows:

"Tannic acid is an alcoholic anhydride of gallic acid, very probably digallic acid."

This structural formula was at first suggested by Schiff:

Gallic Acid.

$$C_6H_2\begin{cases}CO.OH\\OH\\OH\\OH\end{cases}$$

Tannic Acid.

$$C_6H_2\begin{cases}CO.OH\\OH\\OH\\O\end{cases}\qquad C_6H_2\begin{cases}OH\\OH\\CO.OH\end{cases}$$

He subsequently changed this formula to that of an ethereal anhydride, as follows:

$$C_6H_2\begin{cases}OH\\OH\\OH\\CO\end{cases}\Bigg\}\qquad C_6H_2\begin{cases}O\\OH\\OH\\CO.OH\end{cases}$$

Schiff also investigated the reaction, first described by Löwe, of arsenic acid and gallic acid, which the latter considered to be an oxidation. Schiff, however, obtained similar results as with phosphorus oxychloride, and considered it an easier method for obtaining digallic acid, since heating the gallic acid with a dilute solution of arsenic acid was sufficient to effect the conversion. There is, however, considerable difficulty in removing the arsenic from the tannic acid, a portion of the latter being reconverted into gallic acid.

By heating digallic acid as well as a purified natural tannic acid with acetic anhydride, Schiff obtained pentacetyl-tannin, $C_{14}H_5(C_2H_3O)_5O_9$, consisting of warty crystals melting at 137°. This compound is insoluble in water and cold alcohol, but moderately soluble in hot absolute alcohol, and gives no color reaction with salts of iron.

Two years later, in 1873, Schiff published a review of his former work, with the maturer conclusions which experience gave him. He offered the following as the reaction taking place between gallic acid and phosphorus oxychloride:

$$4C_7H_6O_5 + POCl_3 = 2C_{14}H_{10}O_9 + PHO_3 + 3HCl.$$

The tannic acid thus obtained gave a blue-black precipitate with ferric salts, yielded pyrogallic acid on heating, and was converted into gallic acid by the action of dilute acids, without the formation of a trace of glucose. Phosphorus pentachloride and trichloride also converted gallic into tannic acid, but some intermediate and decomposition products resulted.

Schiff also further investigated the action of arsenic acid on gallic acid, and determined that when they are heated together in aqueous solution the change into tannic acid is complete without the arsenic acid undergoing any change. He considered the reaction to be as follows:

$$(1)\ C_7H_5O_4.OH + HAsO_3 = C_7H_5O_4.O.AsO_2 + H_2O;$$

$$(2)\ \left.\begin{matrix}C_7H_5O_4\\AsO_2\end{matrix}\right\}O + C_7H_5O_4.OH = \left.\begin{matrix}C_7H_5O_4\\C_7H_5O_4\end{matrix}\right\}O + AsHO_3.$$

Pure digallic acid was recommended to be prepared

by boiling an alcoholic solution of gallic acid and arsenic acid, the arsenic to be removed from the filtrate by hydrogen sulphide, the solution evaporated to dryness, dissolved in a small quantity of alcohol, ether added in excess, filtered, and the filtrate evaporated to dryness.

In a former paper Schiff supposed he had prepared a trjacetyl and a tetraacetyl derivative of tannic acid, but later investigation convinced him that only the pentacetyl tannin existed, the other compounds being mixtures which resulted from the digallic acid containing some intermediate products with phosphorus.

Schiff at first concluded that "the compound present in the plants which yield tannic acid is probably a very unstable glucoside of polygallic acid, perhaps of the formula indicated by Strecker." "The least purified tannic acid is then the purest, since it contains the largest proportion of sugar."

Later he made the following statement: "That the glucose present in imperfectly purified natural tannin does not exist in the free state is proved by the fact that ether-alcohol and anhydrous alcohol dissolve such tannin freely. Unaltered tannin is probably a glucoside of digallic acid:"

$$C_{34}H_{28}O_{22} = C_6H_{12}O_6 + 2C_{14}H_{10}O_9 - 2H_2O.$$

This formula corresponds with 23 per cent. glucose, and the amount of this substance obtained from natural tannin varies from nothing to 22 per cent., according to the extent to which the tannin has been subjected to purification.

C. Etti in 1884 coincided with Schiff's view of the constitution of tannic acid.

We must conclude, from our present knowledge, that the tannin from galls as found in commerce is capable of being purified until it is simply digallic acid. It is, however, rarely, if ever, found in this condition, but contains variable amounts of glucose in weak combination; therefore tannic acid as we know it is either a glucoside of digallic acid or a mixture of this glucoside with variable proportions of digallic acid.

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